63 - 4 - 1

OREGON METALLURGICAL CORPORATION

Albany, Oregon

EVALUATION OF MOLYBDENUM METAL

PRODUCED BY THE TIN REDUCTION

OF MOLYBDENUM DISULPHIDE

FINAL REPORT

April 13, 1963

Contract NOrd 18124

Contract NOw-62-0754-c

Final Report on Both Contracts

Department of the Navy
Bureau of Naval Weapons
Washington 25, D. C.

TABLE OF CONTENTS

I. INTRODUCTION

This report is a final summary report concluding this project and presenting all pertinent information evolved from tin reduction of molybdenite studies.

Work was begun in April, 1958, on scaling up a laboratory operation for producing low carbon, low oxygen molybdenum metal from molybdenum disulfide and culminated in March, 1963. A high temperature furnace (hot zone 1250°C - 1350°C) had to be designed and fabricated for this special purpose along with a special gas atmosphere purification system. All of the early work centered around furnace and purification train construction with innumerable problems centering around materials of construction for a furnace and reactor retort. The three problems of major consequence were containing tin, corrosion of furnace components by sulfur and high temperature in a sealed high purity gas atmosphere. The work done solving these problems evolving a useable system for producing pilot plant quantities of molybdenum metal by the Nachtmann Poole process is described along with an evaluation of the metal produced.

Thermodynamic considerations behind this process are discussed along with theoretical processing advantages. In addition, the possible enhancement of physical properties of molybdenum due

. OREGON METALLURGICAL CORPORATION

to lowering interstitial impurities (primarily carbon and oxygen) is discussed. In particular, the degree of possible improvement to be expected in interstitials removal by producing molybdenum from a sulfide rather than an oxide is discussed.

A summary of all pilot plant work to date, including data gathered, is presented along with a section including conclusions drawn.

OREGON METALLURGICAL CORPORATION

II. THERMODYNAMIC CONSIDERATIONS IN THE
DESULFURIZATION OF MOLYBDENITE

During the laboratory phase of the work on desulfuriza-
tion of molybdenite with tin a review was made of the various
methods that could be employed for desulfurizing molybdenite.
A brief summary of this work is included here.

Figure 1 is a reproduction of the free energy tempera-
ture relationships for the metal sulfides by Richardson and
Jeffes. The upper one-third of the diagram contains the metal
sulfides to be discussed further. There are several rather
obvious methods that immediately come to mind for desulfurizing
molybdenite such as hydrogen reduction, carbon reduction, lead
reduction, tin reduction, and thermal dissociation. This figure
was included for orientation since most workers are familiar
with this work.

OREGON METALLURGICAL CORPORATION

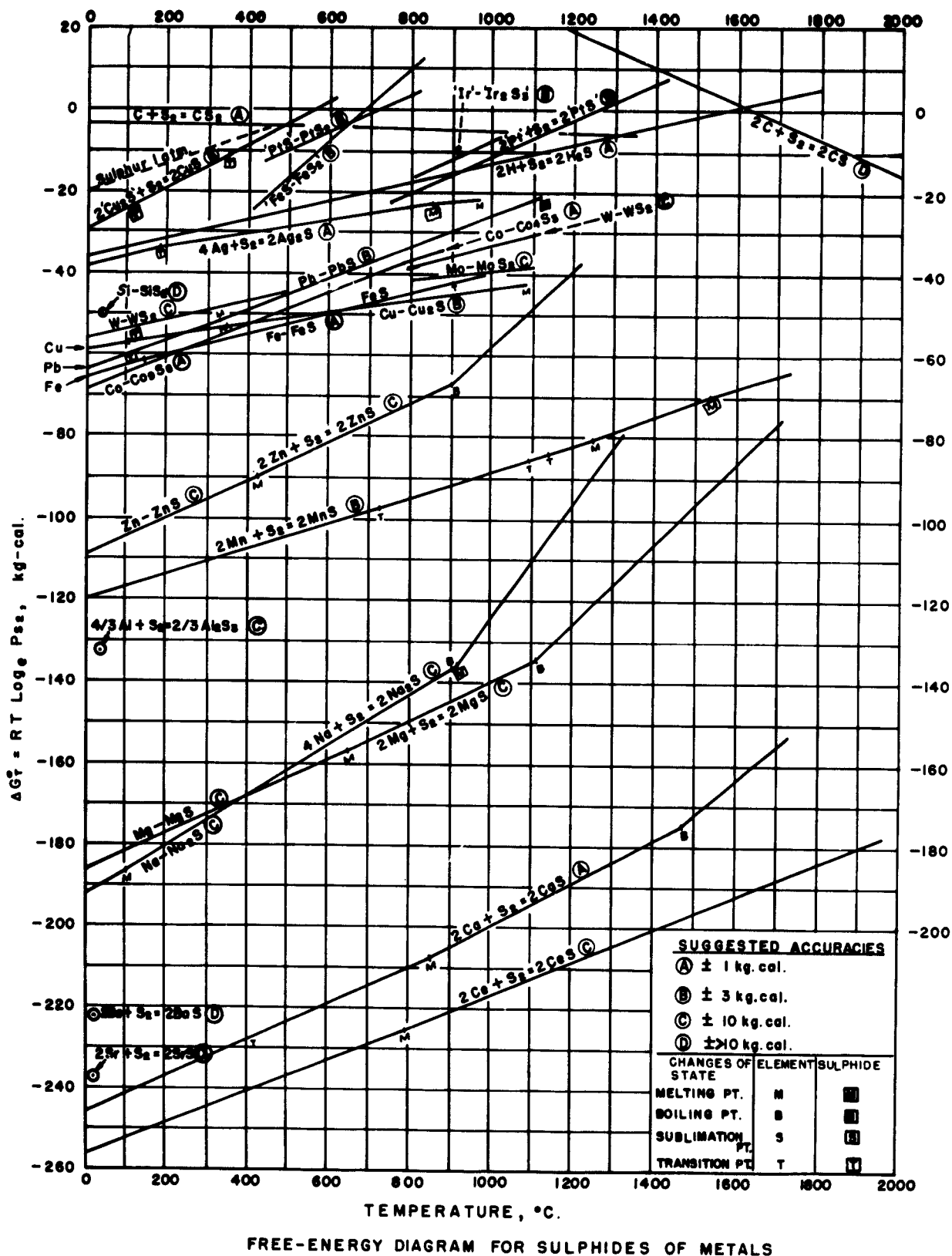FREE-ENERGY DIAGRAM FOR SULPHIDES OF METALS

Figure 1

Figure 2 is a free energy-temperature diagram of most of the above gaseous sulfides. This essentially is a magnified view of the upper area of figure I excluding the sulfides of no interest. Carbon desulfurization from this diagram would seem to be a high temperature reaction, which in fact is the case, for carbon reacts slowly with molybdenum sesquisulfide (Mo_2S_3) all the way up to the temperature where thermal dissociation is predominant. Carbon also forms a refractory carbide with molybdenum making this type of reduction nonusable. Tin, lead, and zinc form stable sulfides and do not form refractory compounds with molybdenum. Of these three tin reduction would appear to be the most promising to desulfurize molybdenite for lead and zinc both have a significant vapor pressure in their respective desulfurizing temperature ranges, and tin does not. Also, molybdenum is wetted very easily by tin and migrates by capillary action quite fast at 1250°C into molybdenum powder enhancing reaction rates.

OREGON METALLURGICAL CORPORATION

-5-

FREE ENERGY – TEMPERATURE DATA
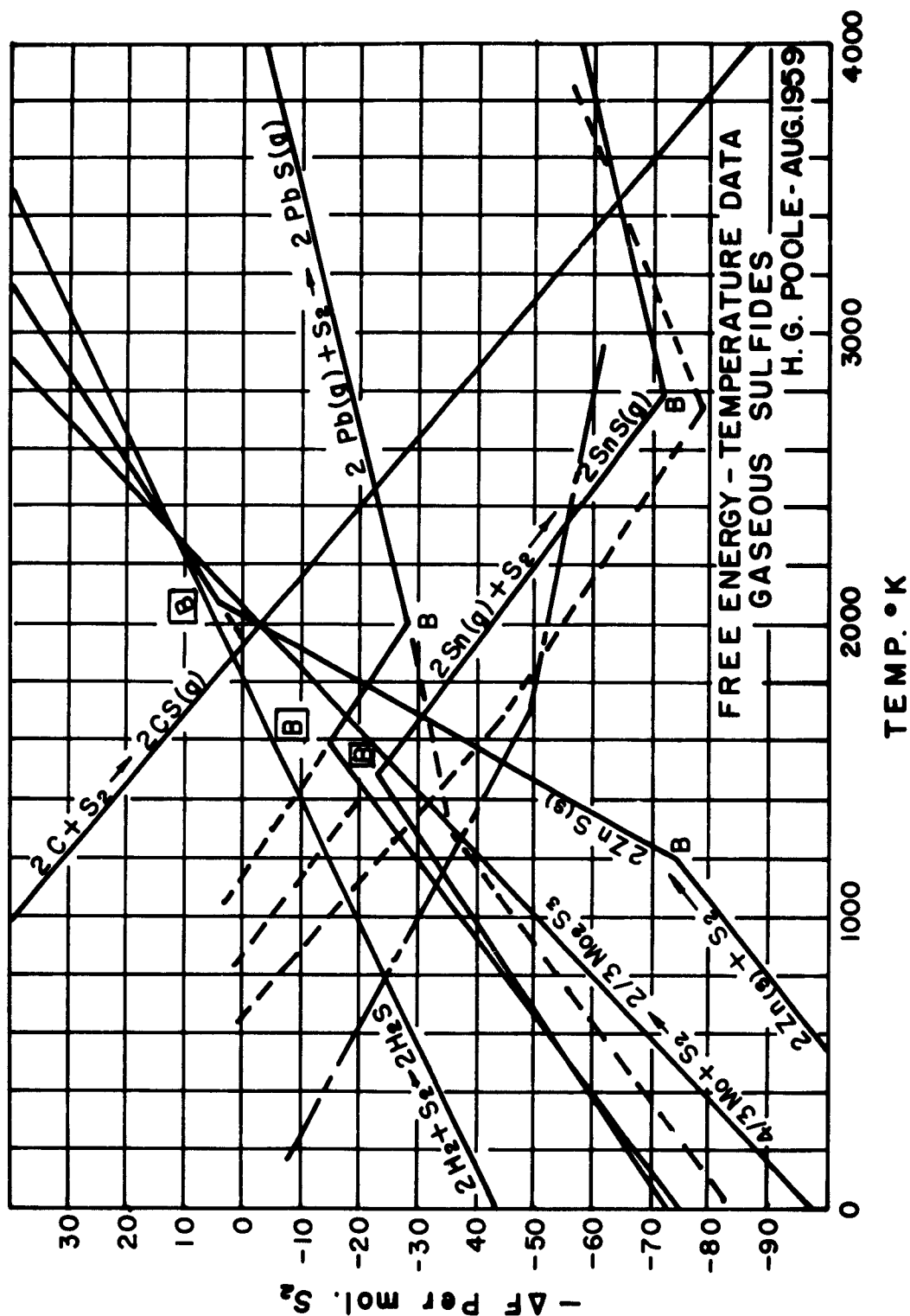GASEOUS SULFIDES
H.G. POOLE – AUG.1959

Figure 2

-6-

Figure 3 is a free energy-temperature diagram for de-
sulfurization of molybdenite. The four curves of primary
interest are: thermal dissociation of molybdenite (MoS_2) to
molybdenum sesquisulfide (Mo_2S_3), tin reduction of molybdenum
sesquisulfide, hydrogen reduction of molybdenum sesquisulfide
and thermal dissociation of molybdenum sesquisulfide.

Molybdenite thermally dissociates in an oxygen-free
atmosphere rather easily to molybdenum sesquisulfide and sulfur
above 1000°C. Figure 3 shows that this should be the case and
that in a hydrogen atmosphere system molybdenum sesquisulfide
is likely to be hydrogen reduced below 1545°C. Above 1545°C,
however, the predominant or rate determining reaction is likely
to be thermal dissociation of molybdenum sesquisulfide and not
hydrogen reduction,

Below 955°C molybdenum sesquisulfide in the presence
of tin and hydrogen is more likely to be hydrogen reduced.
Above 955°C, tin reduction is more likely to become the predom-
inant or rate determining reaction over both hydrogen reduction
and thermal dissociation.

OREGON METALLURGICAL CORPORATION

FREE ENERGY—TEMPERATURE RELATIONSHIP
FOR MOLYBDENITE DISSOCIATION
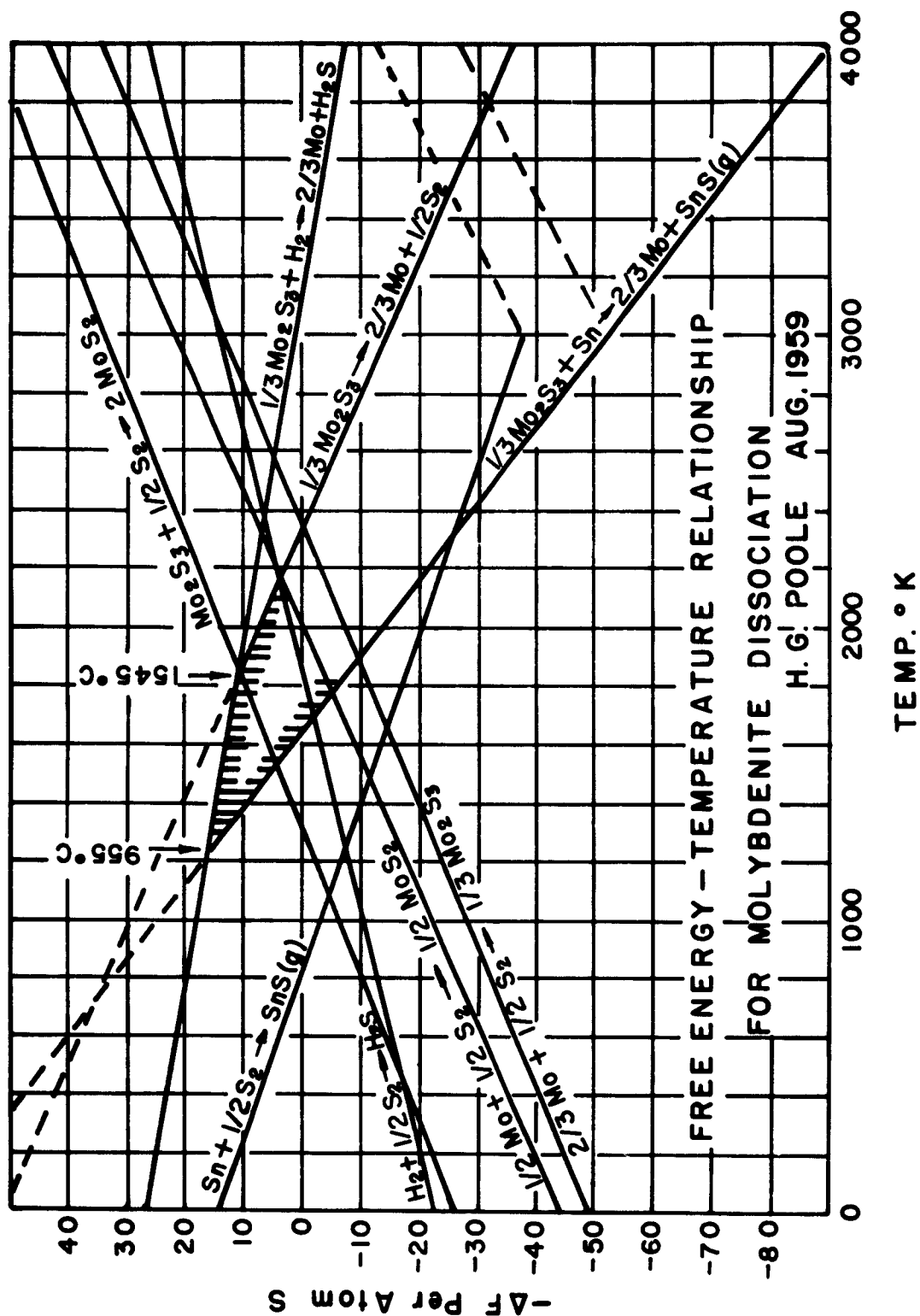H. G. POOLE   AUG. 1959

Figure 3

Figure 4 is a partial pressure-temperature diagram of the possible species present in the desulfurization of molybdenite in a hydrogen atmosphere system. The following curves are shown:

   a.   partial pressure of molybdenum

   b.   partial pressure of tin

   c.   partial pressure of H_2S (from $Mo_2S_3 + 3H_2 \rightarrow 2Mo + 3H_2S$)

   c.   partial pressure of sulfur (from $2Mo_2S_3 \rightarrow 4Mo + 3S_2$)

   e.   partial pressure of SnS (from $Mo_2S_3 + 3SN \rightarrow 2Mo + 3SnS$)

The same information may be seen as outlined in the free energy-temperature diagram (Figure 3) in regard to the most likely reaction to occur at each temperature. In addition, it is most interesting to note that the phases most likely to be present at each reaction temperature in each of the three systems of interest can easily be seen. For example, at 1250°C, in the tin, molybdenum sesquisulfide system the phases probably present are:

   1.   solid molybdenum

   2.   liquid tin

   3.   solid molybdenum sesquisulfide

   4.   gaseous stannous sulfide

   $3Sn + Mo_2S_3 \rightarrow 2Mo + 3SnS$

The three components of this system are:

   1.   molybdenum

   2.   tin

   3.   sulfur

OREGON METALLURGICAL CORPORATION

Applying Gibbs' Phase Rule it may be seen that this system is univariant and thus temperature dependent.

$$F = C-P + 2$$
$$F = 3-4 + 2$$
$$F = 1$$

A tremendous amount of information is contained in Figure 4 and this diagram can not be overemphasized, for experimentally it has been verified that it depicts exactly the situation which actually exists in each instance described. By carefully studying this diagram one can pick out all of the most probable reactions, the temperature at which these reactions are more likely to have an appreciable rate, which reactions are more likely to be predominant over others at any one temperature, the stability of the reaction products with temperature, the stability of the reductants with temperature, the phases probably present in each system at any temperature, etc. Virtually the entire story, thermodynamically speaking, can be seen in these diagrams.

In regard to the tin reduction of molybdenite reaction, note the system is univariant, thus this system could be controlled with temperature control. In practice this is true, thus verifying that this is a univariant system.

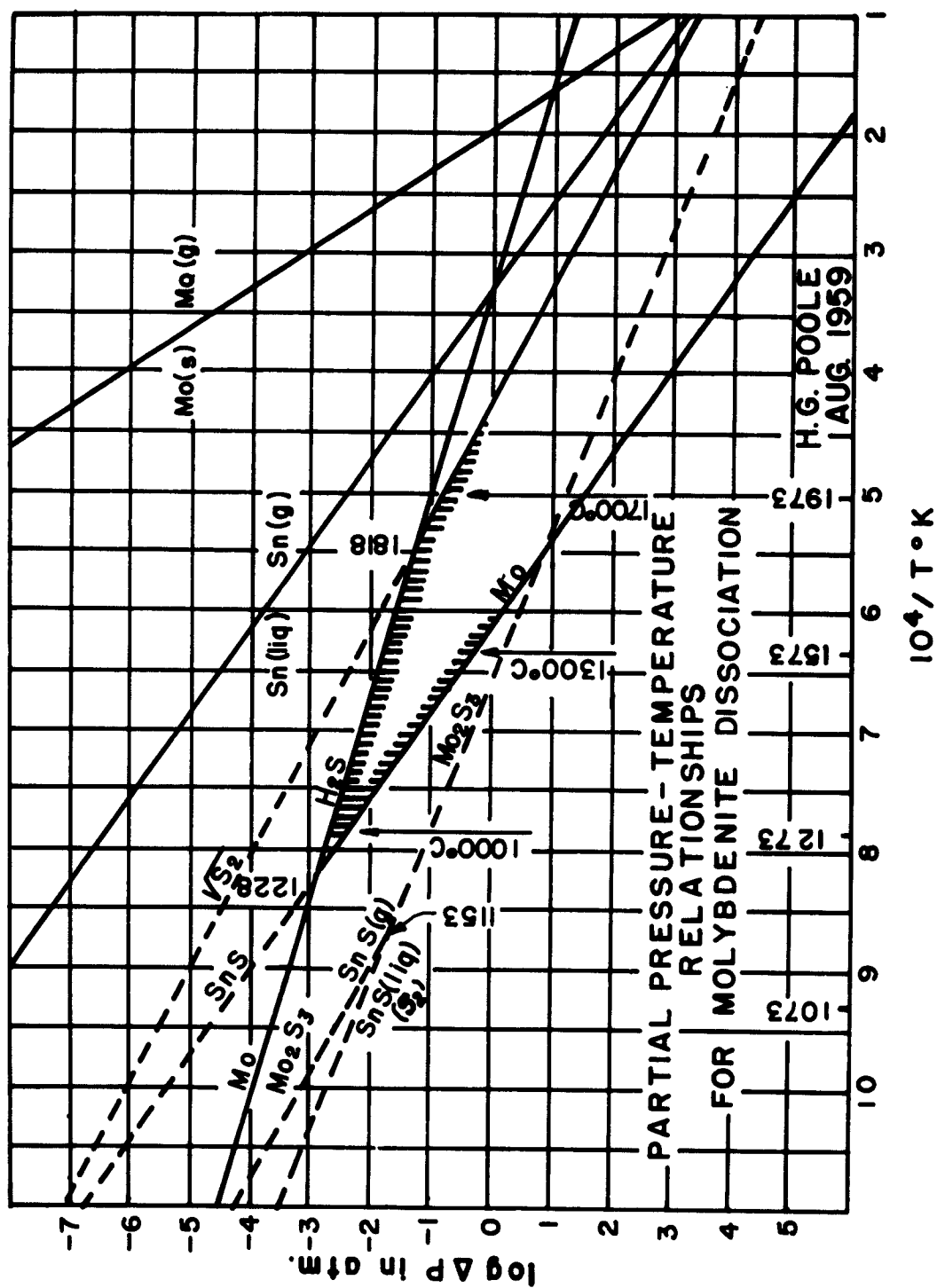OREGON METALLURGICAL CORPORATION

Figure 4

-11-

III. EARLY PILOT PLANT WORK UP TO 1962

(PRIOR TO NOw-62-0754-c)

The early work done can be divided into three basic sections: molybdenite purification, design and operation of the processing system to desulfurize molybdenite, and evaluation of the molybdenum metal produced.

Phase I - Molybdenite Purification

Purified Climax Grade II molybdenite containing oils of flotation was used for most of the laboratory scale work. It was found in the laboratory that a lower carbon content metal could be obtained if the molybdenite concentrate was purchased after oil flotation processing and previous to oil removal by commercial destructive methods called "roasting". The residual oils (carbon) could be more completely removed by acid leaching and hydrogen distillation. Also, the acid leaching purification process was perfected in the laboratory to the point that this was the only necessary purification procedure prior to use.

All of the pilot plant work has been done using both Kennecott Grade II molybdenite and Molybdenum Corporation of America Grade I molybdenite purchased after oil flotation processing and prior to oil removal. Two independent sources were purposely chosen to evaluate purification methods. In order to

OREGON METALLURGICAL CORPORATION

make a process of this kind economically feasible, all sources of molybdenite should be amenable to processing with equal ease and considered on an equal basis as a source of supply of raw materials.

Purification of the molybdenite concentrate is essentially a two step operation. The first step is removal of oils by either solvent extraction or hydrogen distillation. The Kennecott concentrate was amenable to solvent extraction and the Molybdenum Corporation of America concentrate was not. The latter concentrate was placed in a sealed stainless steel retort fitted with an oil trap condenser and means to purge the system with hydrogen under positive pressure. The retort was heated to 750°C and purged for 6 hours to distill oil from each concentrate load. This oil-free dry concentrate is ready for upgrading by acid leaching.

Figure 6 is a photograph of the molybdenite acid leaching facility. A paddle type stirring motor over an elevated 30-gallon polyethylene drum was used to thoroughly mix suspended molybdenite continuously during acid leaching. A polyethylene Buchner funnel connected to a polyethylene water aspirator and PVC drain line was used to remove acid and rinse dissolved impurities from the concentrate.

The acid leaching solution consists of 16 per cent by weight hydrochloric acid, 35 per cent by weight hydrofluoric

OREGON METALLURGICAL CORPORATION
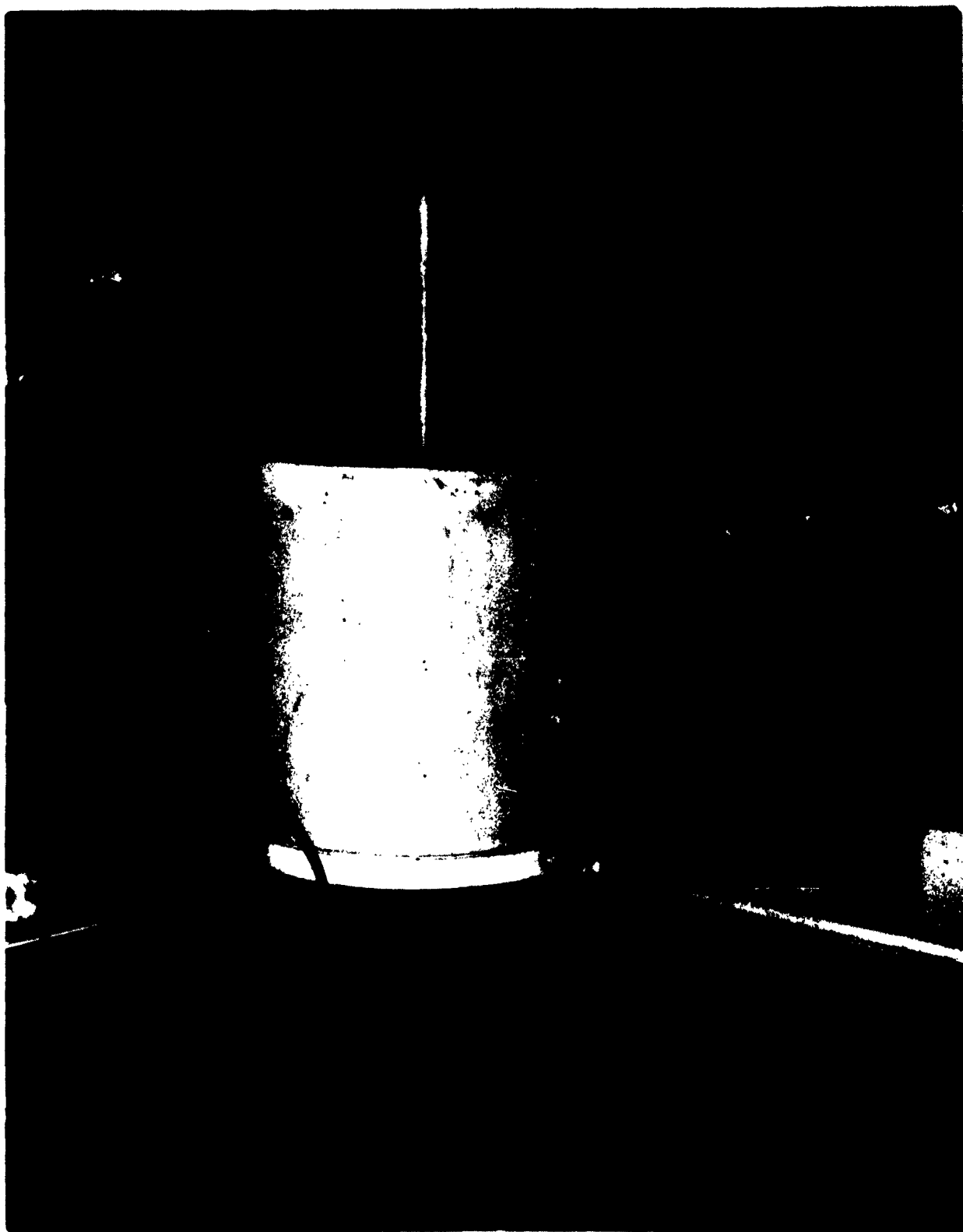
Figure 5

Molybdenite Acid Leaching Facility

acid and the balance water. A liquid balance of about 100 pounds of dry concentrate per 20 gallons of liquid seems to pulp up quite well. All equipment in contact with the leaching solution throughout processing is polyethylene due to the high hydrofluoric acid content. About 100 pounds of dry molybdenite is added to 20 gallons of leaching solution and the mixture agitated for 24 hours. The mixture is then filtered, rinsed with tap water, and dried in an oven 24 hours at 150°F. This material is sampled and the sample converted to metal by the tin reduction process for complete analysis or analyzed directly. The metal conversion allows a carbon analysis to be run along with other impurity analyses.

The primary impurities in molybdenum concentrate as received are oxides of silicon, magnesium and aluminum and sulfides of copper and iron. The two latter impurities have not concerned us too much in the overall process, since they are distilled from ingots during consumable arc melting conversion. The oxide fraction dissolves quite easily unless spinel ($MgO.Al_2O_3$) is encountered. Spinel approaching 1 per cent has been found in some concentrates, and is entirely absent in others. Unfortunately, this spinel is not soluble in any acid mixture tried. However, this impurity can be lowered to a tolerable level by electrostatic processing prior to acid leaching. Figure 6 is a diagramatic sketch of the electrostatic

OREGON METALLURGICAL CORPORATION

-15-

separator equipment used to remove spinel from Kennecott Grade II
molybdenite. The dry oil-free concentrate is fed through a hopper
onto a negatively charged cylindrical drum. The concentrate is
rotated near a positively charged rod at a predetermined distance
from the drum. Each particle of material on the drum is held with
a different strength depending upon the type of conducting mater-
ial. Several knife blade diversion plates are positioned to
collect the fractions coming from the rotating drum. The gangue
material being nonconducting in relation to the molybdenite is
separated in one fraction and discarded. These residual oxides
are of extreme importance, for if present will not reduce during
tin reduction of molybdenite and, if present in sufficient
concentrations, literally explode or break electrodes during
arc melting due to vapor products evolved. If arc melting can
be done on lower spinel concentration material, a high oxygen
molybdenum metal product is formed.

Tables I, II, III, and IV indicate the degree of upgrading
found by acid leaching and electrostatic separation of molybdenite.
Note in Table I that analyses are also compared to laboratory
processed molybdenite produced by H. Gordon Poole's group at
Golden, Colorado.

OREGON METALLURGICAL CORPORATION

-16-

FEED HOPPER

DRUM NEG. CHG.

FIELD 1/2" GAP
POS. CHG. WIRE

RECTIFIER
20,000 VOLTS
0.3 AMPS

TWO ADJUSTABLE
KNIFE BLADES

NON CONDUCTOR GANGUE FRACTION

MIDDLE RECYCLE FRACTION

HIGH PURITY CONDUCTOR
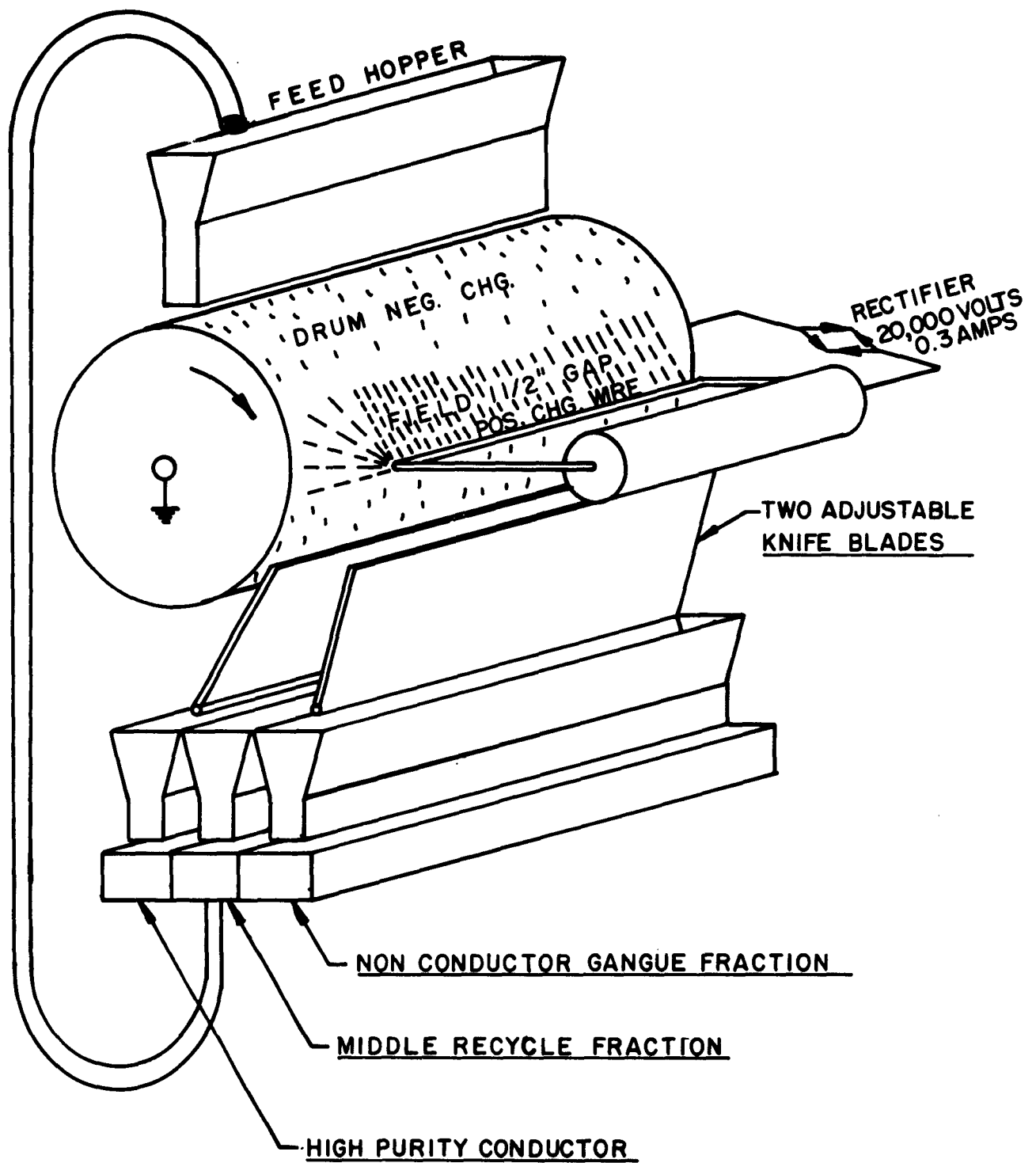
DIAGRAMATIC SKETCH OF AN ELECTROSTATIC SEPARATOR

Figure 6

-17-

TABLE I

Spectrographic Analysis of Acid Leached Kennecott Grade II Molybdenite Concentrate
Fractions in Percent

	Al	Co	Cr	Cu	Fe	Mg	Mn	Ni	Si	Ti	Sn	Ca
Representative Sample	0.15	<0.005	<0.005	0.12	0.04	0.20	<0.005	<0.005	0.005	0.015	<0.005	0.06
+ 60 mesh	0.6	<0.005	<0.005	0.15	0.04	0.6	<0.005	<0.005	0.01	0.015	<0.005	0.20
60 x 100 mesh	0.12	<0.005	<0.005	0.2	0.03	0.15	<0.005	<0.005	0.01	0.015	<0.005	0.03
100 x 200 mesh	0.15	<0.005	<0.005	0.1	0.03	0.2	<0.005	<0.005	0.01	0.01	<0.005	0.04
200 x 300 mesh	0.20	<0.005	<0.005	0.12	0.03	0.2	<0.005	<0.005	0.005	0.015	<0.005	0.08
- 325 mesh	0.25	<0.005	<0.005	0.12	0.05	0.25	<0.005	<0.005	0.005	0.03	<0.005	0.10
Poole Leached*	0.06	<0.005	<0.005	0.08	0.05	0.03	<0.005	<0.005	0.005	0.015	<0.005	0.06

*Material from Golden, Colorado, but analyzed at Oregon Metallurgical Corporation, Albany, Oregon.

TABLE II

Spectrographic and Chemical Analysis of Electrostatically Separated Kennecott Grade II Molybdenite Concentrate Fractions in Percent

	Al	Co	Cr	Cu	Fe	Mg	Mn	Ni	Si	Ti	Sn	Ca
65 x 100 mesh	0.6	<0.005	<0.005	0.5	0.03	1.0	0.005	<0.005	4.5	0.03	<0.005	0.15
100 x 200 mesh	0.1	<0.005	<0.005	0.4	0.04	0.2	<0.005	<0.005	0.7	0.015	<0.005	0.05
200 x 325 mesh	0.12	<0.005	<0.005	0.2	0.04	0.2	<0.005	<0.005	0.4	0.01	<0.005	0.10

TABLE III

Spectrographic Analysis of Kennecott Grade II Molybdenite Concentrate Fractions Electrostatically Separated and Acid Leached in Percent

	Al	Co	Cr	Cu	Fe	Mg	Mn	Ni	Si	Ti	Sn	Ca
65 x 100 mesh	0.04	<0.005	<0.005	0.15	0.06	0.08	<0.005	<0.005	<0.005	0.01	0.03	0.02
100 x 200 mesh	0.05	<0.005	<0.005	0.12	0.04	0.015	<0.005	<0.005	<0.005	0.008	0.04	0.015
200 x 325 mesh	0.15	<0.005	<0.005	0.15	0.05	0.3	<0.005	<0.005	<0.005	0.008	0.04	0.08

TABLE IV

Analytical Values of Acid Leached and As Received
Molybdenite of America Molybdenum Corporation in Per Cent

	Al	Co	Cr	Cu	Fe	Mg	Mn	Ni	Si	Ti	Sn	Ca
As Rec'd	0.15	<0.005	<0.005	0.4	0.04	<0.005	<0.005	<0.005	0.3	0.01	0.005	0.04
Acid Leached	0.005	<0.005	<0.005	0.3	0.03	<0.005	<0.005	<0.005	<0.005	0.01	0.005	0.005

Phase II - Design and Operation of the Process System to Desulfurize Molybdenite

The early phases of this project centered around process equipment design, fabrication and modification. The reduction conditions were such that furnace requirements, reactor requirements, and gas purification requirements were all extremely difficult to achieve. Very little reduction work was done for quite some time while process equipment was evolved.

The first furnace used was a Hevi-Duty globar resistance furnace capable of 1400°C. This proved to be a fine unit and was used throughout most of this early work. A 6' 446 stainless steel retort about 4" I.D. was inserted in the furnace and connected on both ends to a gas recycle purification train, forming a tube furnace. The purification train consisted of a pyrex glass limestone tower, filter, coldtrap, drierite column, recycle pump, and titanium sponge getter furnace at 850°C. Hydrogen was considered to be the best atmosphere for processing so all work was done in a hydrogen atmosphere.

In the first run attempted a number of 3" diameter X 3" high molybdenite-tin briquettes were made and loaded directly into the steel retort at about 1200°C. This reduction attempt ended a total failure.

Tin liquated from the pellets and formed a low melting

OREGON METALLURGICAL CORPORATION

point alloy with steel and sulfur compounds attacked the steel as well. A number of holes appeared in the reactor tube early in the run causing burning hydrogen to come out of the sieve-like hot zone. This tin and sulfur problem had not been recognized in design but proved to be the major problem to overcome.

All new materials of construction available at this time for the tube were surveyed such as cermets, high melting point alloys, etc. but were considered not usable for one reason or another. Coors Porcelain in Golden, Colorado, offered a 4' long X 3½" I.D. gas-tight high purity alundum tube on special order. This was considered the best material for resisting both tin and sulfur. Therefore, a tube furnace consisting of a 446 stainless steel tube with alundum insert was constructed for the globar furnace. In addition, a front loading chamber and exit condenser chamber were added. Figure 7 is a diagramatic sketch of the system as set up for the second trial reduction run. Since copious quantities of tin liquated from pellets quite fast in the first run, it was considered necessary to build molybdenum boats to contain tin in close proximity to pellets in the early phases of reduction. This was done and a second charge tried. A 3" diameter briquette was placed in a boat and charged into the hot zone of the tube furnace with a push rod. The furnace temperature was controlled externally at 1250°C. Tin liquated from the pellet but very little to no

OREGON METALLURGICAL CORPORATION

-22-

Figure 7

-23-
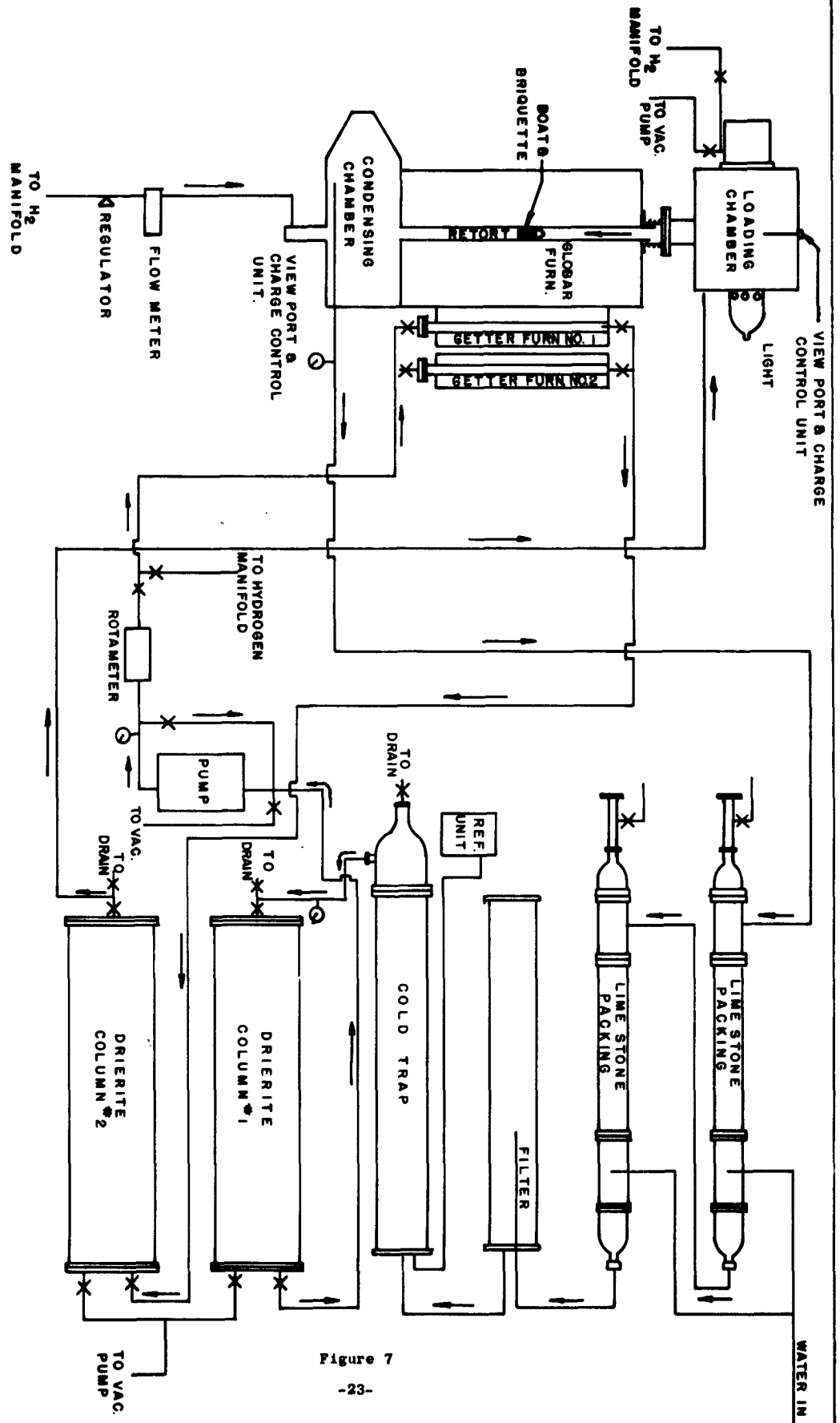
visible reduction was seen (SnS vapor). There was too much heat loss from the outer steel tube to the interior of the alundum tube. Also, hydrogen is a good heat transfer medium and the hot zone was very narrow. A tremendous amount of heat was extracted continuously from the hot zone by hydrogen flow. Also, cold hydrogen had insufficient time to reach hot zone temperatures prior to striking the pellet. This meant that the inner alundum liner must be near 1350°C to achieve around 1250°C at the briquette. From optical pyrometer measurements there appeared to be about a 100°C temperature gradient from the outer steel tube surface to the inner alundum tube surface. The outer steel tube, therefore, would need to be 1450°C to achieve reduction temperatures of 1250°C. Unfortunately, the 446 stainless steel tube was found to fail at 1400°C in a short time due to sofenting and scaling

To solve this problem, a simple molybdenum resistor fashioned from 0.030" ribbon was fabricated and mounted on 1/4" molybdenum rods held in a ceramic insulator to internally heat the hydrogen prior to entering the hot zone. This heating unit, shown in Figure 8, was placed inside the reaction retort tube prior to the reaction zone and a study of the effect of super-heated hydrogen (up to 1600°C) on the system made. The globar furnace was varied in temperature from 1000°C to 1300°C and the heat input of the resistor was varied from 1 KW to 6 KW at 700°C to 1600°C. To sum up briefly our findings, the element performed dramatically well. By turning the power up and down

OREGON METALLURGICAL CORPORATION
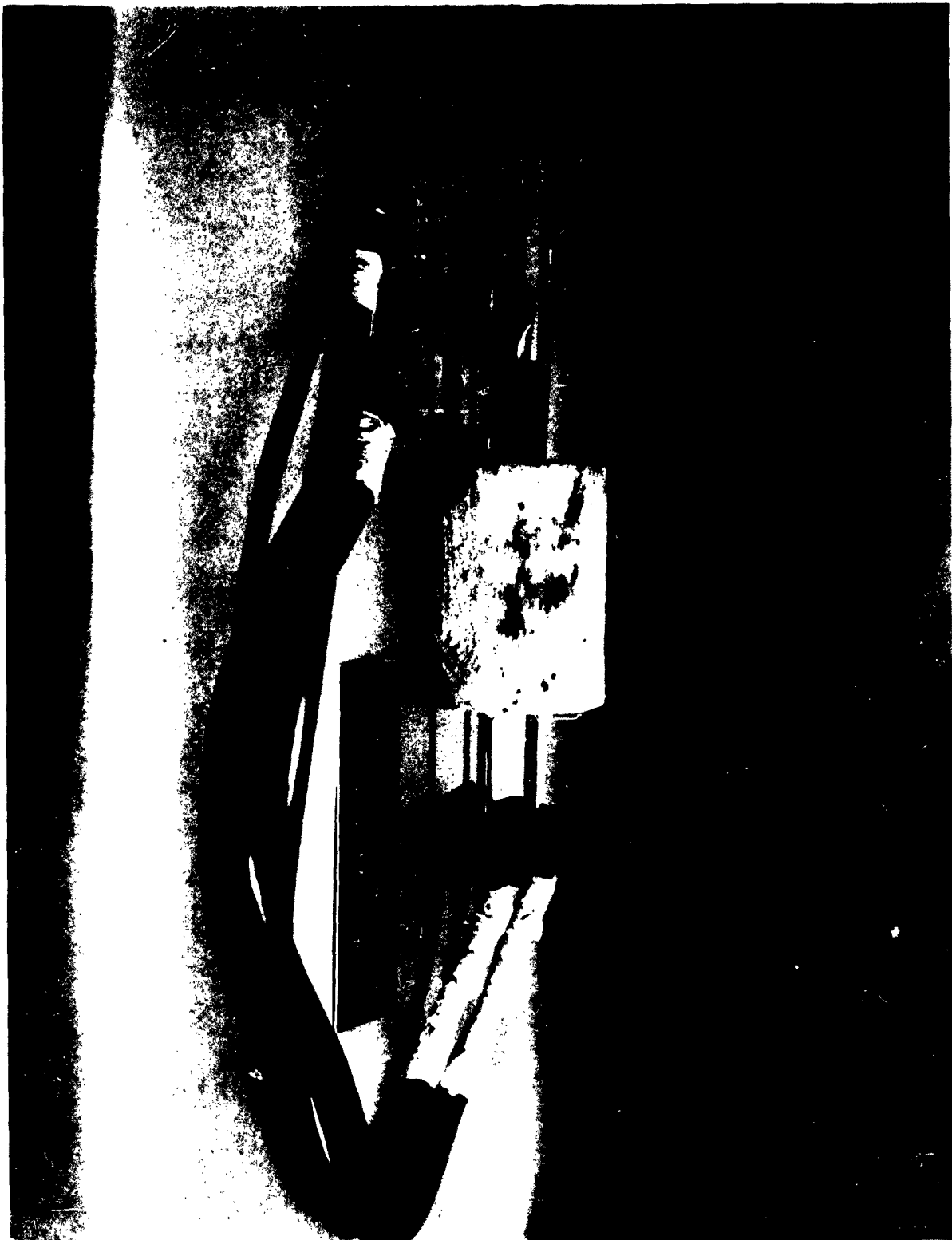
Figure 8

Molybdenum Ribbon Superheater, Showing Flexible Power Leads

on the internal resistor, one could almost instantaneously start
and stop SnS vapor evolution from a pellet in the hot zone.
Since the element was mounted entirely on metal, these tempera-
ture fluctuations did not harm it. A method of achieving both
reduction temperature and heat capacity had been found with a
minimum of external heating through the stainless steel tube.
In fact, the internal resistor worked well enough to permit
turning off the globar and operating on the internal resistor
alone.

A typical reduction run consisted of loading a 3" dia-
meter briquette, contained in a molybdenum boat, into the center
zone of the tubular reactor, pushing the heating element in
after it and applying power. When SnS evolution ceased from
visual observations the heating element was pulled out, followed
by the pellet. Unfortunately, the alundum liner used was heat
sensitive and cracked easily from thermal shock. Invariably
boats would crack and tin would work downward through cracks in
the ceramic tube and on through the steel tube. The system
would then have to be taken apart and a new tube with liner in-
stalled. This replacement was expensive and happened too fre-
quently to make the system usable for gathering data on reduction.

Since the internal resistor worked well, a new furnace
was fabricated to replace the globar unit. A steel shell 3 feet
square and 4 feet long was sealed by welding and filled with
OREGON METALLURGICAL CORPORATION

insulating brick around a 4 foot castable ceramic refractory tube. The furnace was fitted with flanges front and rear to mate with existing condenser and loading chamber flanges. A schematic of this furnace is shown in Figure 9. No metallic or low melting point materials of construction were used in the furnace interior. In this system a flowing stream of hydrogen acts as the heat transfer medium and provides all of the heat necessary for desulfurization. Calculations were made to verify that the volume of hydrogen being recirculated had the heat carrying capacity to desulfurize the charges used and could carry SnS evolved to the condenser. The unit was found to work extremely well.

Purified hydrogen gas was passed through the center of the insulator holder, by the element and heated to about 2200°C, passed to the briquette giving up heat, and the estimated temperature of the hydrogen with evolved reaction products leaving the reaction retort is 1000°C. This amount of heat is passed on to the condenser and thereby wasted as far as reduction is concerned. The hydrogen flow was varied between 250 CFH and 300 CFH depending on the element design and element heating characteristics. All of the good reduction data accumulated was from this system so further discussion of the theory behind this novel method of heating is in order.

OREGON METALLURGICAL CORPORATION

-27-
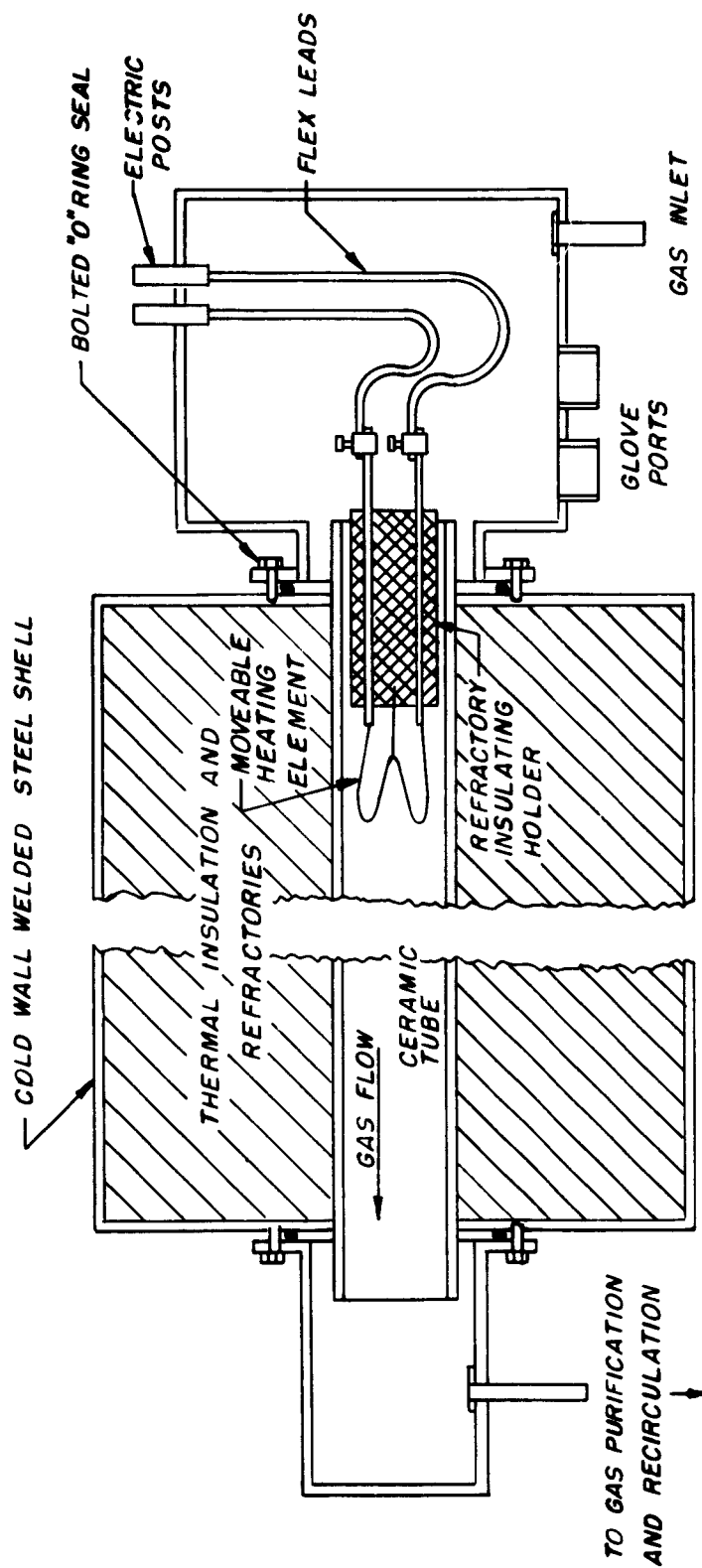
RESISTANCE ELEMENT IN OPERATING POSITION
IN A TUBE REDUCTION FURNACE

Figure 9

The heat carrying capacity of hydrogen varies with the temperature to which it is raised. Therefore, a balance exists between heating element characteristics and hydrogen flow. This can best be illustrated by Table V.

Notice that 250 C Ft. hydrogen has the capacity to carry all of the heat generated by the particular element tested until the element temperature reaches about 2150°C. From this point on, the element temperature increases slowly with increased power input and the element power input surpasses the carrying capacity of hydrogen. In practice we have found when this situation exists, as one might expect, the element melts in a localized area. Therefore, in order to operate this particular element at 2200°C the hydrogen flow rate has to be increased from 250 CFH to near 300CFH. This is the balance that was used in operating this furnace in all of the early work. It is interesting to note that hydrogen is a very efficient heat transfer medium and that from the foregoing data one can determine quite accurately the available maximum heat input for reduction. If the boiling point of SnS is 1230°C, the heat content of 250 C Ft. hydrogen from the element temperature to 1230°C can be determined and this is very near the usable available heat for tin reduction of molybdenum sesquisulfide for heat losses are small in this furnace.

OREGON METALLURGICAL CORPORATION

-29-

TABLE V

TABLE INDICATING THE HEAT BALANCE BETWEEN THE
CARRIER GAS AND THE HEATING ELEMENT IN THE
INTERNALLY FIRED RESISTOR FURNACE

Theoretical Max. Heat Carrying Capacity of H_2/250 CFT

Temp. °C	H_T in KW	$H_T - H_{1200}$ In KW	$H_T - H_{1000}$ in KW	Actual Measurements Made	
				Element Temp. °C	Element KW Input
1000	2.625	-	0.00	1790	2.67
1200	3.175	0.00	0.55	1990	4.17
1500	4.025	0.85	1.40	2070	4.85
1800	4.90	1.725	2.275	2100	5.20
2000	5.50	2.325	2.85	2150	5.79
2100	5.80	2.625	3.175	2160	6.16
2200	6.10	2.925	3.475	2190	6.68
2300	6.41	3.235	3.785	2210	7.08

A brief outline of the tin reduction of molybdenum sesquisulfide process power and heat requirements are shown in Table VI.

The desulfurization rate in tin reduction of molybdenum sesquisulfide is dependent upon the rate of evaporation of SnS from the briquette, and is temperature dependent for it is a univariant reaction. The boiling point of SnS is about 1230°C as near as can be determined experimentally. Notice, from Table V, that in order to saturate the carrier gas with SnS by evaporation at 1227°C or 1327°C the power requirements are 1.16 and 4.33 KW/250CFt/Hr respectively. Table V also pointed out that at a hydrogen flow rate of 250 CFH and a temperature drop from 2200°C to 1200°C hydrogen gas can supply a maximum of 2.925 KW power input available for formation and evaporation of SnS (since requirements for formation of SnS are small, they can be neglected). At 300 CFH flow rate the power input capacity for hydrogen is near 4 KW under similar conditions. From Table VI it can be seen that at 1227°C the power requirements for maximum vaporization of SnS with 250 C Ft. of hydrogen is 4.34 KW (this would be 17.375 lb. of SnS). Since charges actually used contain on the order of 2½ pounds of produced SnS, the furnace element fabricated has the capacity to provide enough heat at a sufficiently high temperature for the desulfurization process. It is significant to realize that a

OREGON METALLURGICAL CORPORATION

TABLE VI

POWER REQUIREMENTS FOR TIN DESULFURIZATION OF MOLYBDENITE IN A FLOWING STREAM OF HYDROGEN

Temperature °C	Carrying Cap. of H_2 (Max.)/1000 CFT. Lb. SnS	BTU/lb Mol Vol		KW/1000 CFT/Hr			KW/250 CFT/Hr	
		H_2 (H_T-H_{25})	SnS (HVap.)	H_2	SnS	Total	SnS	Total
827	0.014	10198	3.31	8.31	.00097	8.311	.0024	2.07
927	0.381	11500	87.2	9.38	.0256	9.406	.0064	2.35
1027	2.900	12880	662.	10.49	.194	10.684	.049	2.66
1127	15.57	14256	3560.	11.62	1.041	12.661	.260	3.16
1227	69.50	15630	15890.	12.75	4.65	17.40	1.16	4.34
1327	258.0	16990	59100.	13.85	17.33	31.18	4.33	7.79

relatively small decrease in power input, gas temperature, or gas flow would be expected to markedly affect the SnS evaporation rate. This was dramatically demonstrated in this particular furnace during operation. By looking through the glass exit sight port down the tube furnace, we could observe SnS evolution from charges during reduction with changes in these variables. This effect also was very advantageous in gathering rate data. It was found that a charge could be inserted in the furnace and the tin reduction reaction begun almost instantaneously after power was turned on the heating element. Conversely, the reaction could be stopped almost instantaneously with power removal. This allowed good reduction rate data to be accumulated.

Figure 10 shows graphically actual reduction rates obtained in the furnace using 250-300 CFH hydrogen flow rate at 6 KW, 6.5 KW and 7 KW power input settings. Briquettes 3" diameter and about 3" long weighing approximately 4 pounds were used for this study. Figure 11 is a photograph of a typical briquette. To enhance rapid evolution of SnS at the briquette core a 5/8" - 3/4" hole was drilled through the center of each briquette. Shown with the briquette is a piece of a 1" X 1" X 15" molybdenum powder bar made from metal produced by the tin reduction process. These bars were

OREGON METALLURGICAL CORPORATION

-33-
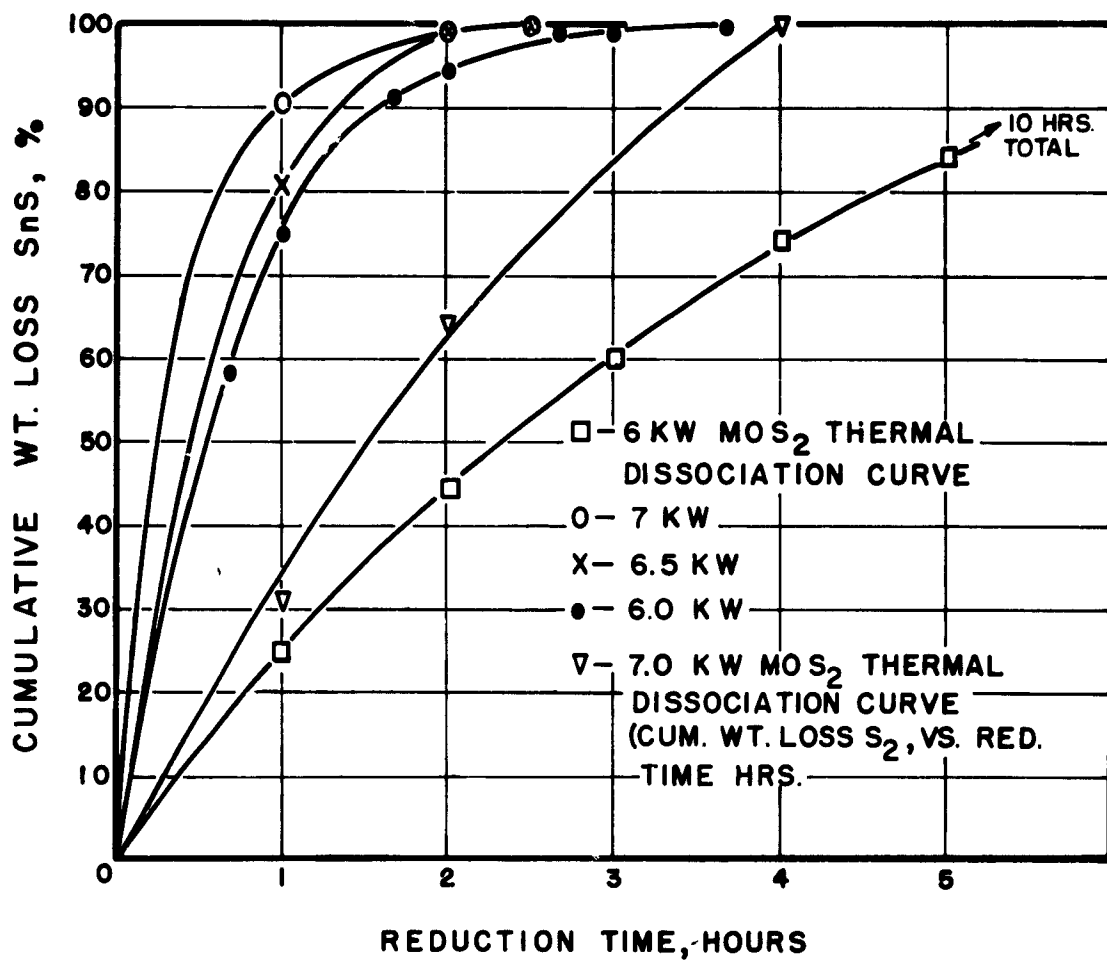
REDUCTION RATE CURVE FOR THE TIN REDUCTION
OF MOS_2 IN THE INTERNALLY FIRED TUBE FURNACE

Figure 10

used as electrode stock for conversion of metal produced to consumable melted arc cast ingots.

As can be seen from Figure 10, a complete tin reduction run, yielding about one pound of loosely sintered molybdenum powder, can be run in a relatively short period of time. Also, reduction times can arbitrarily be varied by choosing an operating temperature and power input. The 6 KW curve shown roughly corresponds to a briquette temperature of 1250°C and the 7 KW curve roughly corresponds to a briquette temperature of 1300°C as measured with an optical pyrometer. Note that raising the reduction temperature 50°C lowers reduction time requirements from four hours to two and one-half hours, substantiating earlier theoretical data presented.

As a point of interest, molybdenite has been thermally dissociated in this tube furnace and rate data has been included in Figure 10 for informational and comparative purposes. Note that molybdenite could be thermally dissociated in about 10 hours using a 6 KW power input (about 1600°C - 1650°C briquette temperature) and in four hours using 7 KW power input (about 1700°C briquette temperature).

One can see from this data that a reasonable rate of reaction can be chosen for either desulfurization process and

OREGON METALLURGICAL CORPORATION

this rate will then dictate the conditions of furnace operation. The exact requirements for any given desulfurication job outlined can be predicted from data presented.

It should be noted also that a flowing stream of pure gas, such as hydrogen, devoid of sulfur-containing vapor products evolved during desulfurization of molybdenite, has the same theoretical rate efficiency as a vacuum system as far as removal of sulfur-containing gaseous reduction products is concerned. Therefore, theoretically, the rate of reaction in both vacuum and pressure systems should be comparable. Enough data has been compiled to substantiate this experimentally and state that in fact desulfurization rates in vacuum, in a flowing inert gas system and in a flowing hydrogen system are equivalent. The rather obvious advantages inherent in above atmospheric pressure furnace equipment systems such as the one fabricated for this process makes a circulating gas system appear more desirable and economical. This is particularly true with the large variety of new fine gas purification units on the market.

There probably are more convenient gas purification units on the market today than the train that was fabricated for purifying hydrogen in this study, but this train incorporated the best units found at this time. A dual set of wet

OREGON METALLURGICAL CORPORATION

-36-

Figure 11

Molybdenite-Tin Briquette and Molybdenum Powder Sintered Bar

limestone scrubbing towers were used for initial roughing of
H_2S formed and entrained SnS fines removal. A cold trap operating
at -32°F was used in the second stage to remove the bulk of the
water added to the gas stream in stage 1. The third stage was
drierite to remove water to low levels. The final fourth stage
was the heart of the purification train. It consisted of titanium
sponge contained in a 6" diameter retort 4' long heated to 850°C.
All gaseous impurities were removed to very low levels in this
unit. Table VII shows the type of impurities removed by titanium
sponge gettering.

TABLE VII

ANALYSIS OF A SAMPLE FROM 9 POUNDS OF TITANIUM SPONGE USED IN THE
GETTERING FURNACE FOR ONE WEEK DURING PRODUCTION OF 40 POUNDS OF
MOLYBDENUM POWDER, PPM

	C	H	O	N	S
As Received Sponge	20	11	1270	80	50
Used Sponge	3700	20300	8450	2580	10300

The impurity pickup was considered gross in the above
particular instance and getter charges were increased in size and
changed more often. When oxygen reached about 3000 PPM, sponge
was changed. This took about one week in the larger system. A
mass spectrometer gas analysis of good recycle gas showed 99.9

OREGON METALLURGICAL CORPORATION

molecular per cent hydrogen with the bulk of the remainder hydrogen sulfide and traces of carbon monoxide and nitrogen. Table VIII shows a mass spectrometer gas analysis of hydrogen taken at the time the sponge with analysis shown in Table VII was changed.

TABLE VIII

MASS SPECTROMETER FURNACE HYDROGEN ANALYSIS IN MOL. %

Hydrogen	99.6609
Hydrogen Sulfide	0.1557
Carbon Monoxide	0.1418
Nitrogen	0.0338
Carbon Dioxide	0.0048
C_4 + Hydrocarbons	0.030
Water	Nil
	100.0000

This correlates with the sponge analysis showing that carbon monoxide, nitrogen, carbon dioxide and hydrocarbons are produced during reduction and can effectively be removed in the getter furnace to low levels. Hydrogen sulfide being present in larger concentrations from hydrogen reduction can not be removed as effectively as the other impurities. However, this would only mean small sulfur pickup during furnace cooling would occur in molybdenum powder produced and hydrogen sulfide wasn't

OREGON METALLURGICAL CORPORATION

-39-

really of any concern at levels encountered in this particular process system. Analyses of furnace hydrogen do definitely show a high purity furnace atmosphere was produced using the purification train fabricated for this purpose. The train did leave room for improvement, however, for frequent regeneration of components was time consuming and relatively expensive.

At this point in the project, an accidental fire destroyed the entire research and development area containing all of the molybdenum research facility equipment. Since the internally fired furnace destroyed worked so well, it was decided to build a complete new facility with this principle in mind. A large furnace 4' X 4' X 4' was fabricated with a rectangular center reaction tube about 7" X 5" X 4' with four resistance heaters coming in horizontally on the sides. The recycle gas can be passed around the hot resistors, heated to 2200°C and then passed to the center rectangular tube where it makes a right angle turn toward the exit end of the furnace. This superheated gas thus carries all of the heat necessary for the tin reduction of molybdenum sesquisulfide and carries SnS evolved to a condenser chamber at the exit end of the furnace. This furnace design allows charging and discharging without removing resistor heating elements as in the previous furnace fabricated. Tungsten was found superior to molybdenum,

OREGON METALLURGICAL CORPORATION

-40-

columbium, and tantalum for resistors, so was used in all subsequent work.

There was never enough working and storage area in the old equipment, so very large chambers were built to encase the furnace on two sides and on the front. Rubber glove ports were fabricated in four areas making four separate working areas. The two side chambers were primarily for storage and element replacement. Elements invariably burn out and new ones could be bolted into place relatively easily since purified furnace gas recirculates through all of these working areas. The front chamber with two glove port working areas was primarily for charging the furnace and storage of molybdenum powder produced. Since high purity gas was recycled through all chambers, no elaborate storage containers were necessary to store metal powder to minimize oxidation.

Figures 12, 13, 14 and 15 are photographs showing the furnace fabricated. Recycle gas inlet connections and power inlet connections were placed on top of the furnace. The main gas recycle supply was divided in half with each half going to a side chamber working area and then on into the side resistor port of the furnace. A small amount of gas was metered into the front chamber to prevent back diffusion of SnS from

OREGON METALLURGICAL CORPORATION

-41-
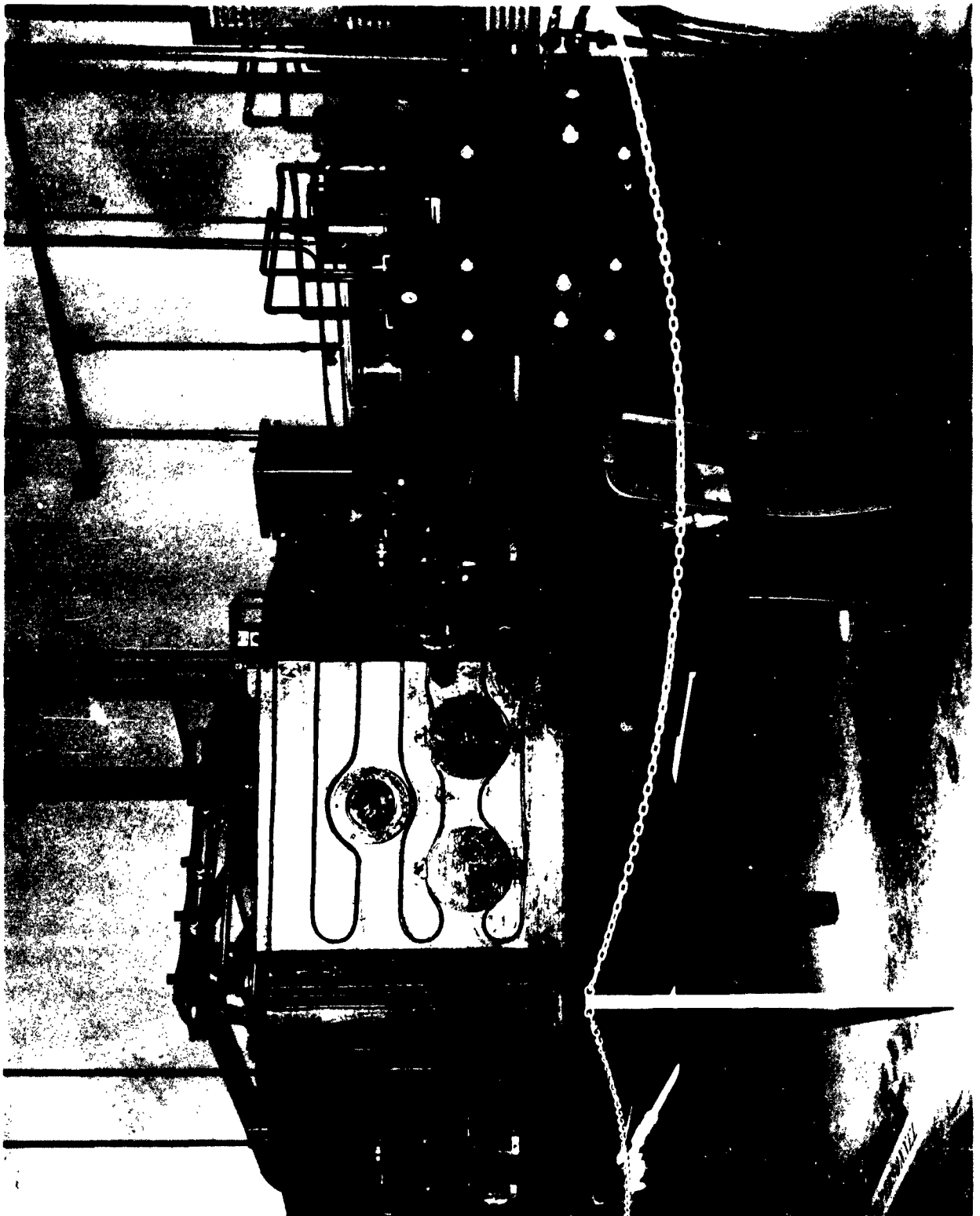
Figure 12

Overall View of Molybdenum Facility
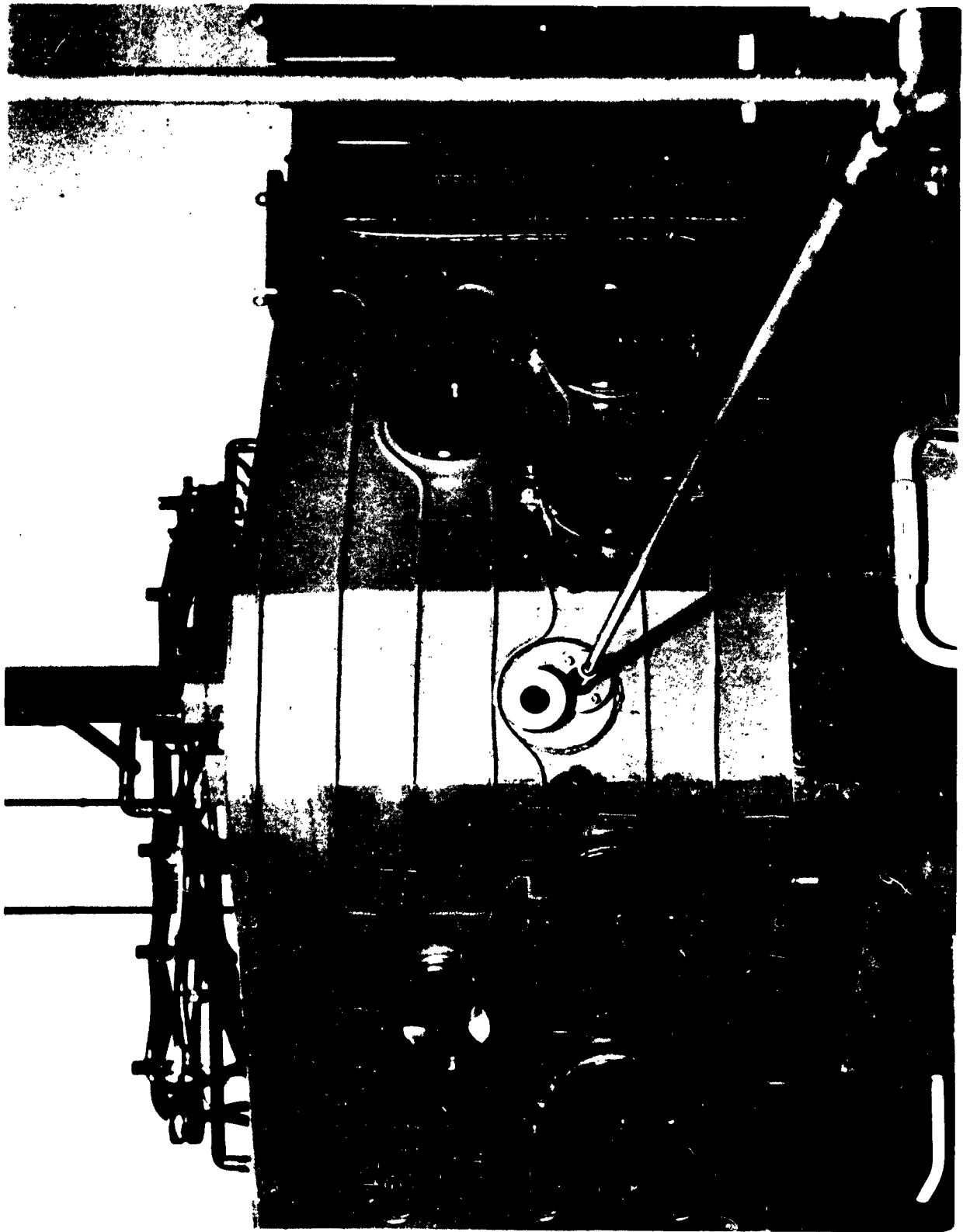
Figure 13

Front of Molybdenum Facility Reduction Furnace

Figure 14

View Inside of the Front Working Area of the Reduction
Furnace Unit Showing Molybdenum Powder Storage Containers
and Mortar with Pestle

Figure 15

Power Linkage to Tungsten Heating Elements in the Reduction
Furnace

-45-

the furnace reaction chamber. Since the system was operated under positive pressure cover plates were fabricated for all glove ports. A water cooled push rod seen in Figure 12 was used to push boats containing charges into the hot zone and remove molybdenum metal produced. Since the furnace hot zone was operated at 1350°C and the hot zone was very close to the front chamber, a series of cooling coils were soldered to the outer steel shell for operator comfort when working through rubber gloves.

The purification train fabricated was more elaborate than the previous one. The water scrubbing towers containing limestone were eliminated because of the problem of continuously removing water efficiently to very low levels and the labor involved in maintaining water at a constant level as pressure in the system fluctuates. A baghouse type of filter with wool flannel leaves was used to remove micron particle size SnS entrained in recycle gas. The bulk of the SnS dropped out in a large condenser chamber on the back of the furnace, but a good deal of entrainment of SnS was noted. This was removed prior to gas purification.

A cold trap was used for the first stage of purification. Missimers, Incorporated, constructed a two-stage Freon 22-ethane

cascade unit capable of cooling 1000 CFH flow of hydrogen continuously to at least -130°F. This unit was operated at about -140°F and removed water and high molecular weight hydrocarbons primarily. Some H_2S was also removed.

The second stage of purification was Linde Molecular Sieve Pellets. Two columns about 1' diameter by 6' high were constructed so that one could be used while the other was being regenerated. Type 6A pellets used removed CO_2, H_2S, H_2O, CO and low molecular weight hydrocarbons to reasonably low levels.

The third stage of purification was a Deoxo converter containing palladium on aluminum oxide pellets. This unit converted any free oxygen to water in a hydrogen atmosphere system by catalysis.

The fourth stage of purification was another set of two Linde Molecular Sieve Pellet columns identical to those used in the second stage. These columns removed any water formed in the converter and further lowered CO_2, CO. H_2S and low molecular weight hydrocarbons.

The fifth and final stage of purification was titanium sponge gettering. Two furnaces with retorts 8" O.D. X 4' long were fabricated so that one could be used while the other was

OREGON METALLURGICAL CORPORATION

-47-

being regenerated. Recycle gas was heated to 850°C in contact with titanium sponge and then passed through a water cooled heat exchanger to be cooled prior to entering rotameters. This stage removed trace quantities of CO_2, CO, H_2O, N_2, O_2, H_2S and hydrocarbons. Impurities not taken out by the other units were removed here (if regeneration of one unit was not done at the proper time for example). This was by far the most important part of the purification train. Figures 16 and 17 are photographs showing the purification train components fabricated.

Figure 18 is a photograph showing the panel used to achieve a constant pressure in the system during operation. A constant pressure regulator behind the panel had an adjustable pressure valve which was set at 3 3/4 PSIG during most of this work. The gas regulator was connected to a flow meter to get a measurement of the make-up gas usage. This flow meter was used very little, for little or no make-up gas was used. However, in the event of pin-hole leaks, a rise in the make-up gas usage could be noted. The system could then be leak-checked and cleaned up prior to further reduction studies.

Four saturable reactor power supply units were used to operate the four tungsten resistors. The power units are shown in Figure 16 on top of the cold trap and the operating panel shown in Figure 19. Each unit was capable of a maximum of 400 amperes at 30 volts but was run at about 6-7 KW or 24-28 KW total power.

OREGON METALLURGICAL CORPORATION
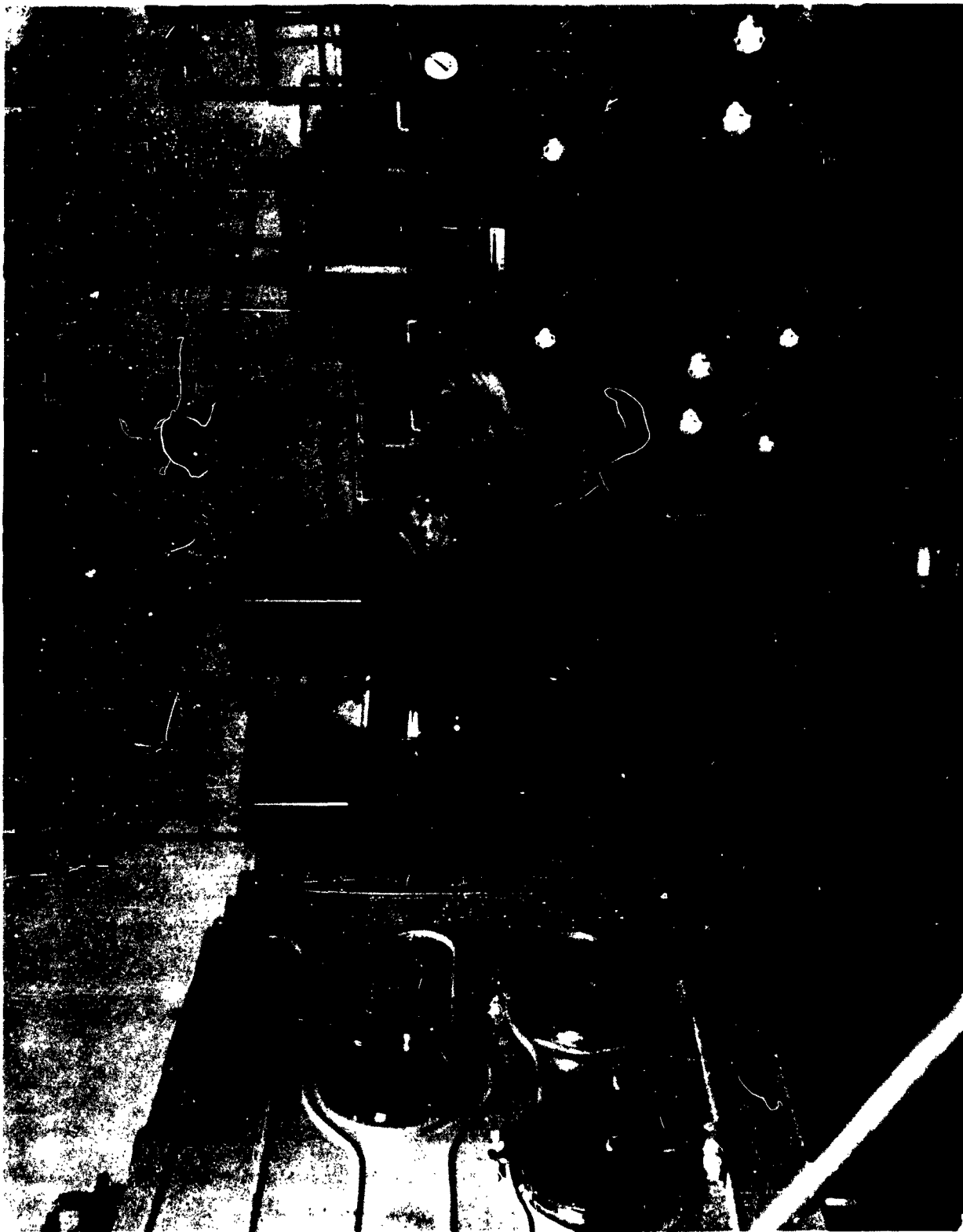
Figure 16

Molybdenum Facility Showing Saturable Reactor Power
Supply, Cold Trap, Molecular Sieve Columns and Deoxo
(behind the panel).
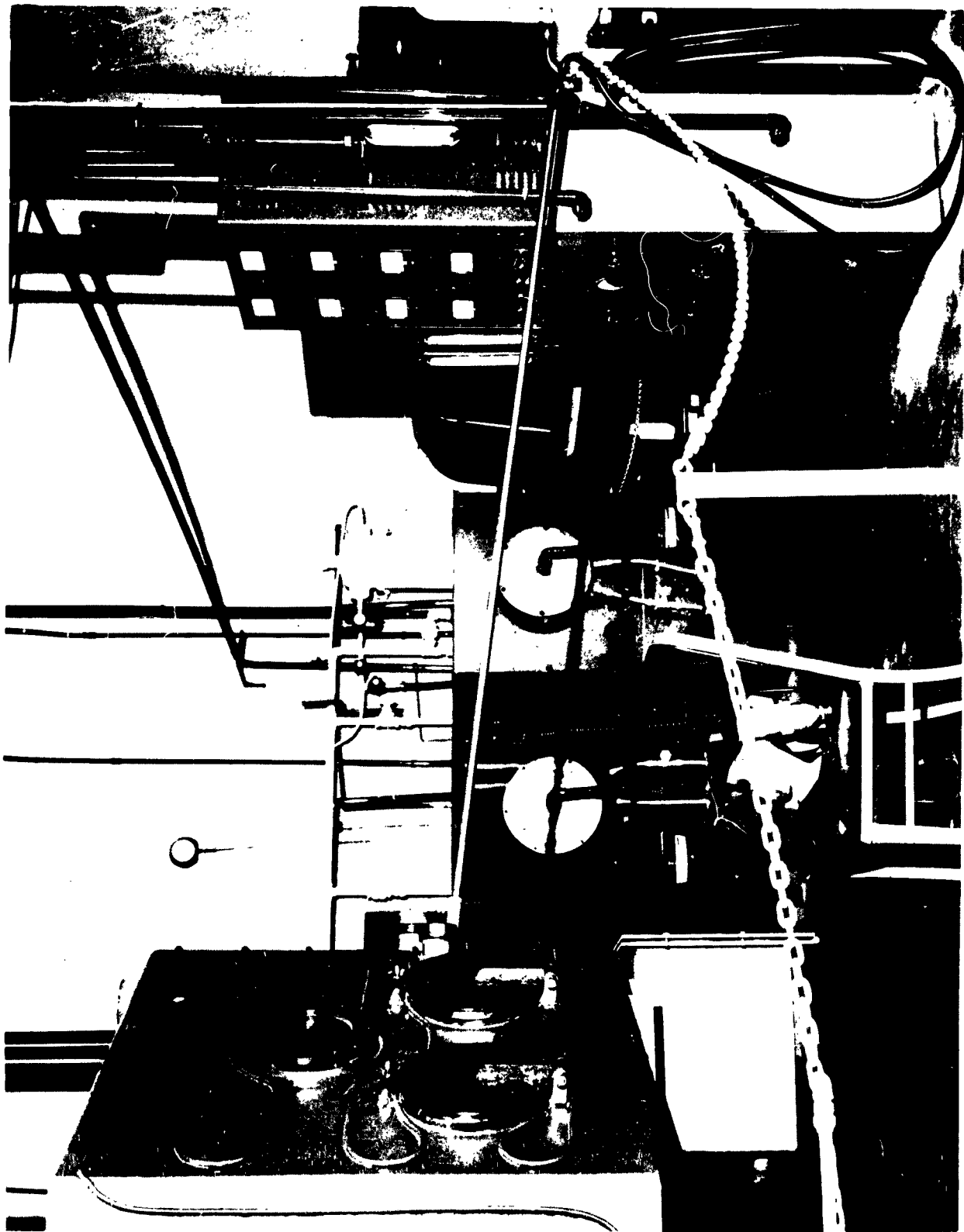
Figure 17

Molybdenum Facility Showing Two Purification Furnaces,
Reduction Furnace, Power Control Panel and Gas Flow
Control Panel

-50-
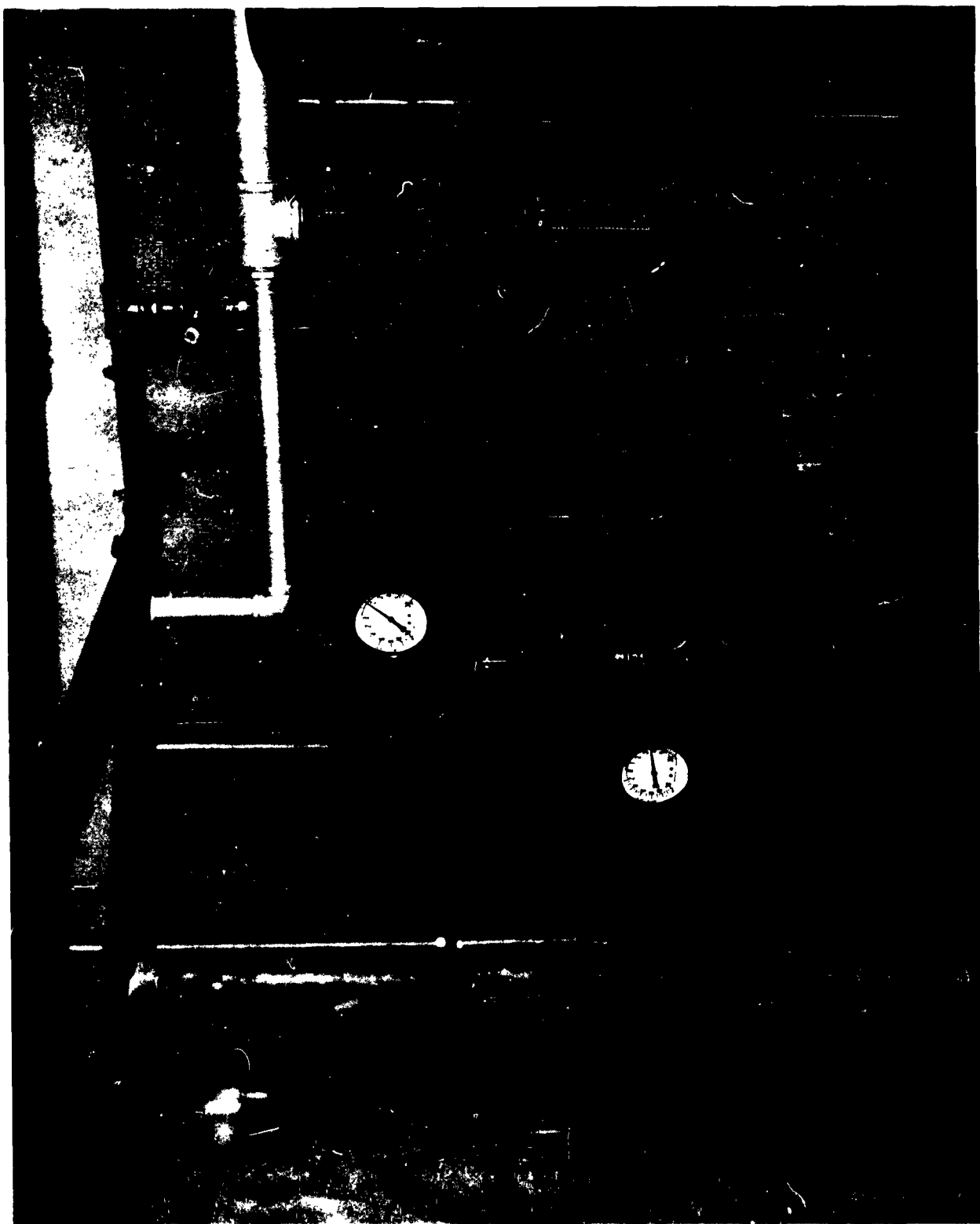
Figure 18

Pressure Control Panel for Molybdenum Facility
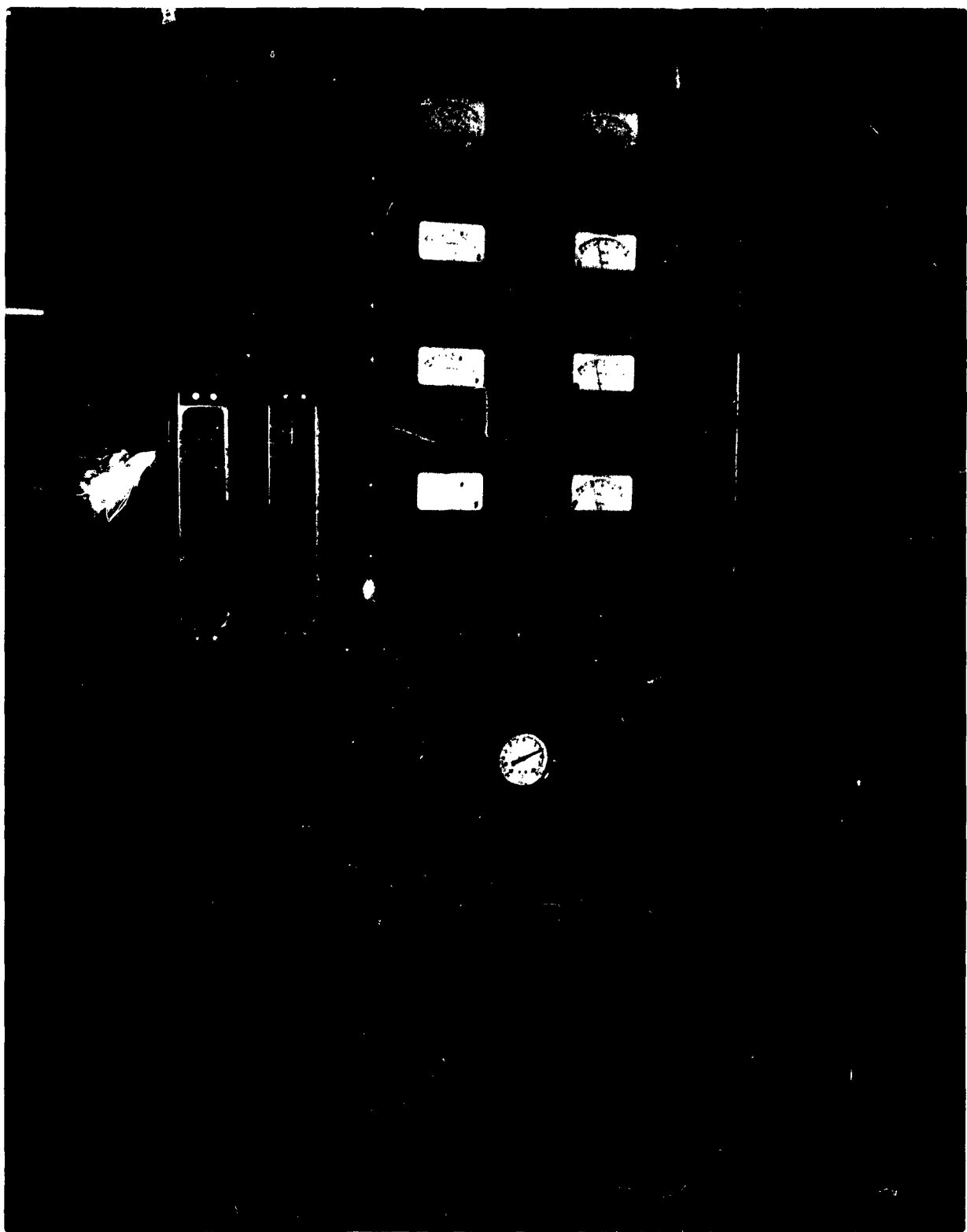
Figure 19

Molybdenum Facility Power Control Panel and Gas Flow
Control Panel

The process system and process background information has been described in some detail. The reduction sequence is extremely simple. A 3" diameter by 3" tall briquette of molybdenite and tin is made. This briquette is placed in a molybdenum boat, pushed into the furnace hot zone, left for six hours and pulled out of the hot zone into the front furnace working area. At this point the sesquisulfide has been desulfurized and molybdenum metal produced. The metal produced is in the form of powder loosely sintered into the shape of the original 3" diameter briquette. This sintered shape is struck with a pestle a few times to crumble the product into small pieces. These pieces are stored in glass jars or cans in the furnace until enough metal has been made to form an ingot. The metal conversion is done by conventional consumable arc melting procedures.

Table IX is a brief resume of the processing requirements for the tin reduction of molybdenite process.

TABLE IX

PROCESSING REQUIREMENTS FOR TIN REDUCTION OF 2# BATCHES OF MoS_2

IN AN INTERNALLY FIRED FURNACE

1) Purified Molybdenite and Commercially Pure Mossy Tin
2) Purified Hydrogen or Inert Gas (H_2O, CO_2, CO, H_2S, O_2, N_2, Hydrocarbons removed)
3) Reaction Zone Temperature of at least 1250°C plus 6.0 - 7.0 KW Available Power Input
4) Exit SnS Heated to at least 1000°C to Condenser
5) Micron and Submicron SnS Particles Removal Prior to Recycling Gas

OREGON METALLURGICAL CORPORATION

Phase III. Evaluation of Metal Produced Prior to NOw-62-0754c

Table X illustrates the typical purity of molybdenum
produced in pilot plant equipment prior to Navy Bureau of Weapons
contract NOw-62-0754c. All samples were arc melted so values
are comparable.

The first two samples, labeled OREMET A and OREMET B,
are from tin reduction of molybdenite runs. These two particular
runs were picked to illustrate the variance or extremes observed
in typical carbon and oxygen values. One sample is lower in
oxygen than carbon and the other is lower in carbon than oxygen.
Note that in both cases the combined oxygen plus carbon is 54 PPM
or less. In carbon deoxidation of molybdenum by commercial methods
combined barbon plus oxygen is normally double to triple this much
(100-150 PPM). The second two samples in Table X were included
for comparative and informational purposes and were from thermal
dissociation runs in the internally fired resistor furnace. The
last two samples shown labeled Published Thermal Dissociation A
& B, were from arc cast ingots made from molybdenum powder pro-
duced by the thermal dissociation of molybdenite in vacuum. This
metal was made in the Climax Molybdenum Company of Michigan
vacuum furnace and the analytical values listed are from their
published data. It is interesting to note that the analytical
values of molybdenum produced by thermal dissociation of molyb-
denite in the flowing gas system and vacuum system are similar.

OREGON METALLURGICAL CORPORATION

TABLE X

COMPARISON OF ANALYSIS OF MOLYBDENUM MADE BY TIN REDUCTION OF MoS2 PROCESS

WITH ANALYSIS OF THERMALLY DISSOCIATED MoS2 PROCESS METAL

Chemical Impurities in Parts Per Million

Lot Number	Carbon	Oxygen	Nitrogen	Sulfur	Tin	Titanium	Silicon
OREMET A (Tin Reduced MoS2)	9	45	30	0	50	50	50
OREMET B (Tin Reduced MoS2)	20	10	20	0	50	150	50
Thermal Dissociation OREMET A	20	110	20	40	50	50	50
Thermal Dissociation OREMET B	20	50	20	60	50	80	50
Published Thermal Dissociation A	160	6-5	3	30	--	45	32
Published Thermal Dissociation B	10	55-51	3-4	20	--	45	32

Also, as mentioned previously, desulfurization rates are similar. This bears out theoretical calculations made on the process.

Figure 20 is a photograph of buttons used as standards to visually inspect for high carbon and/or high oxygen. Molybdenum powder in a 10-pound lot was sampled and a button made by non-consumable arc melting methods. The surface of the button after melting could be used to give an indication of purity. With increasing carbon content the surface tension decreases but fluidity also decreases and the surface becomes frosty. With gross oxygen contamination the button is very fine grained, frosty and metal flows away from the arc. This simple visual examination was used in all of the early laboratory work to separate good runs from bad runs simply and inexpensively and to get a quick idea how various changes in processing affected the end product. Further, cracking the high purity buttons with a hammer and looking at grain boundaries under 400X - 800X gives a further indication of purity. Carbides and oxides show up clearly and one can get a quantitative estimate of carbon and oxygen content easily and quickly. In some cases, this estimate is better than analytical values when either carbon or oxygen is below 50 PPM. This method has proven very reliable and simple for following changes in oxygen and carbon throughout reduction.

OREGON METALLURGICAL CORPORATION
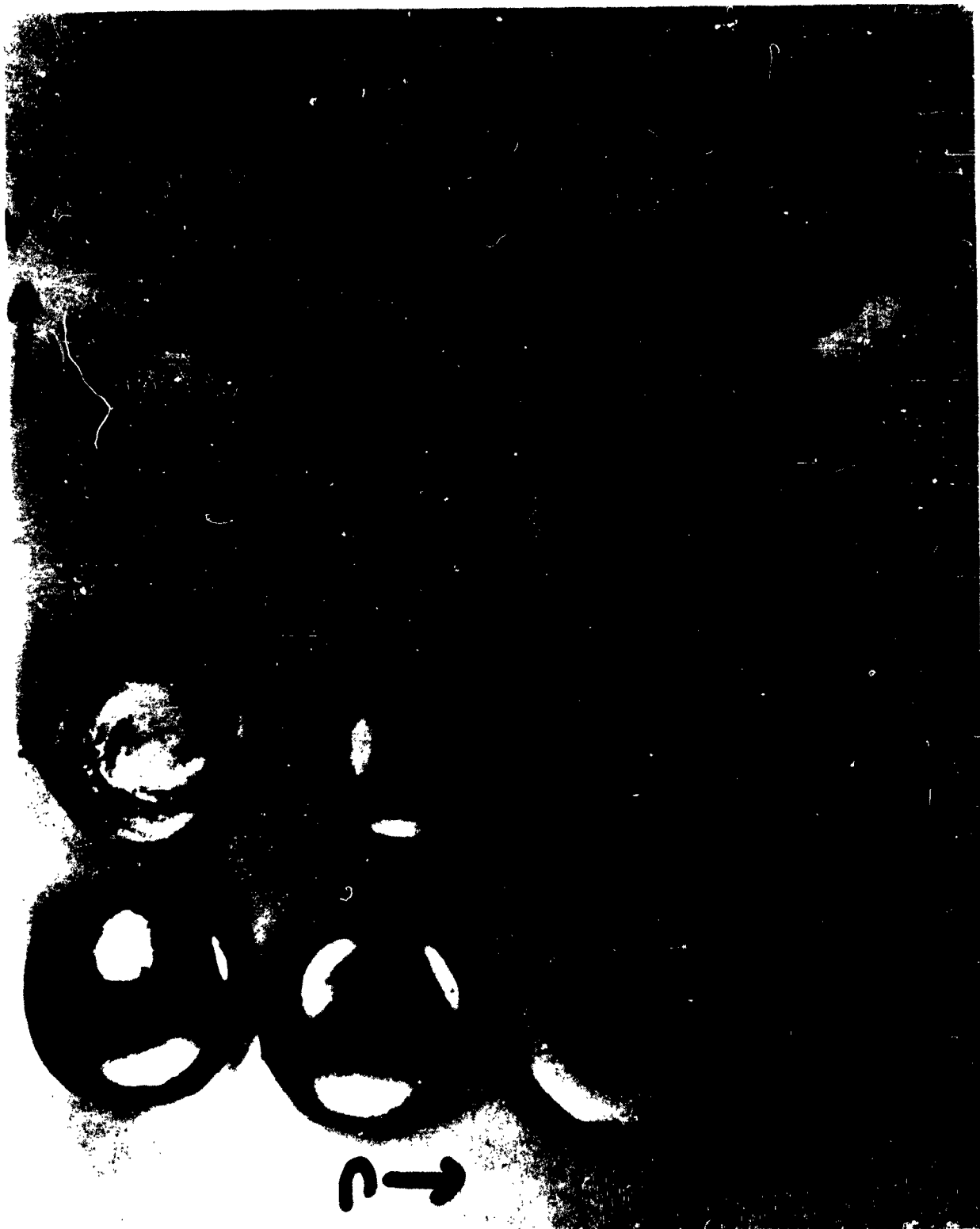
Figure 20

Metal produced in this work that was less than 50 PPM carbon plus oxygen was found to be quite ductile. Small scale fabricability tests indicated that direct conversion of arc cast ingot material to plate by either upset forging or rolling could be done successfully. Very little metal was available for testing and project funds were almost exhausted at the time of this testing, thus limiting the work that could be done in this area. Figures 21, 22, and 23 are photographs showing visually specimens converted directly from consumable arc cast ingot material. All specimens deformed easily without grain boundary failure or cracking. Dye check showed no surface defects opening up and no edge cracking on hot worked pieces. This limited study indicated low oxygen-low carbon as cast molybdenum ingot material had excellent fabricability characteristics.

OREGON METALLURGICAL CORPORATION
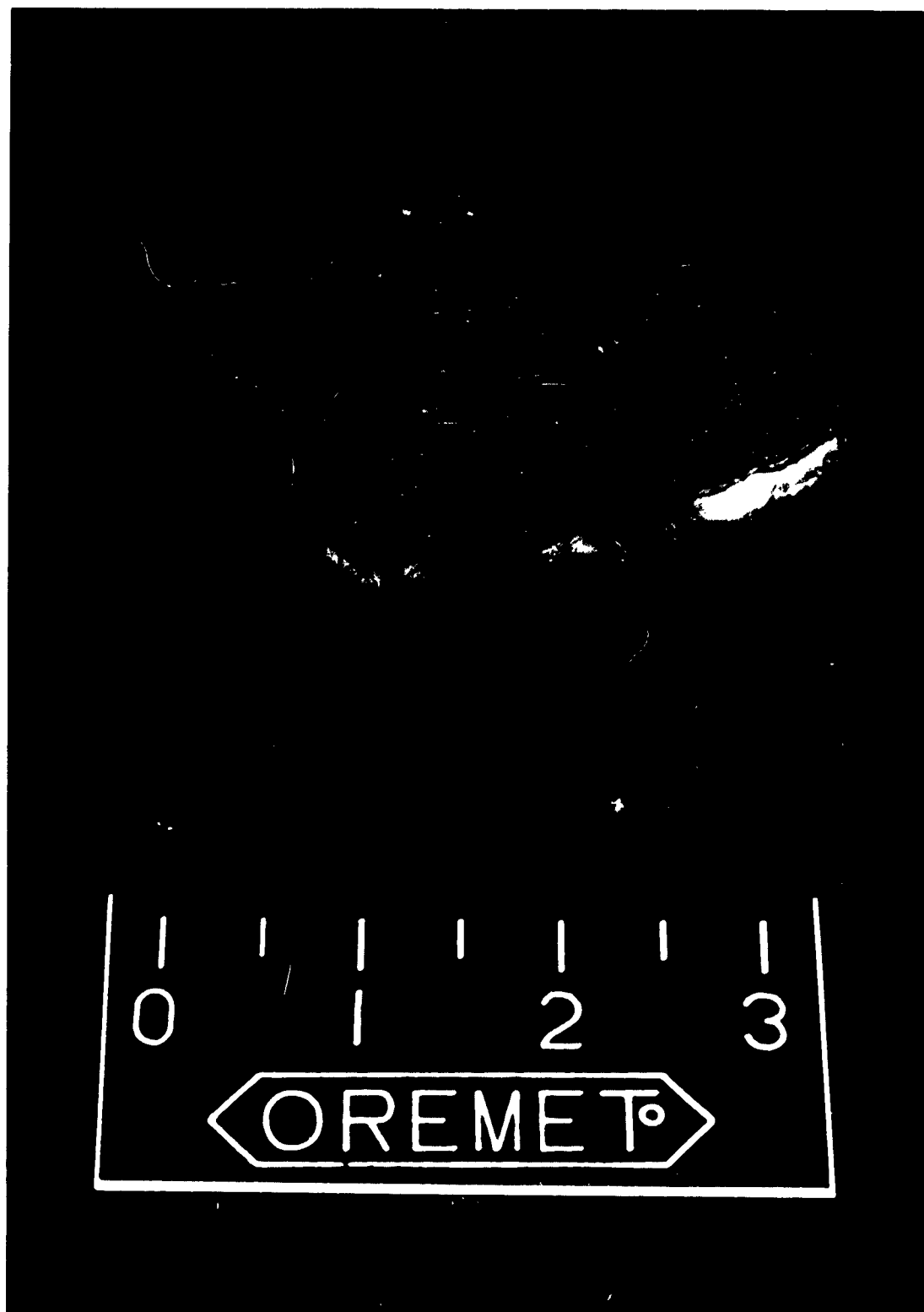
Figure 21

Molybdenum Specimen Hammer Forged from 0.560" to 0.279"
from As-Cast Ingot Material
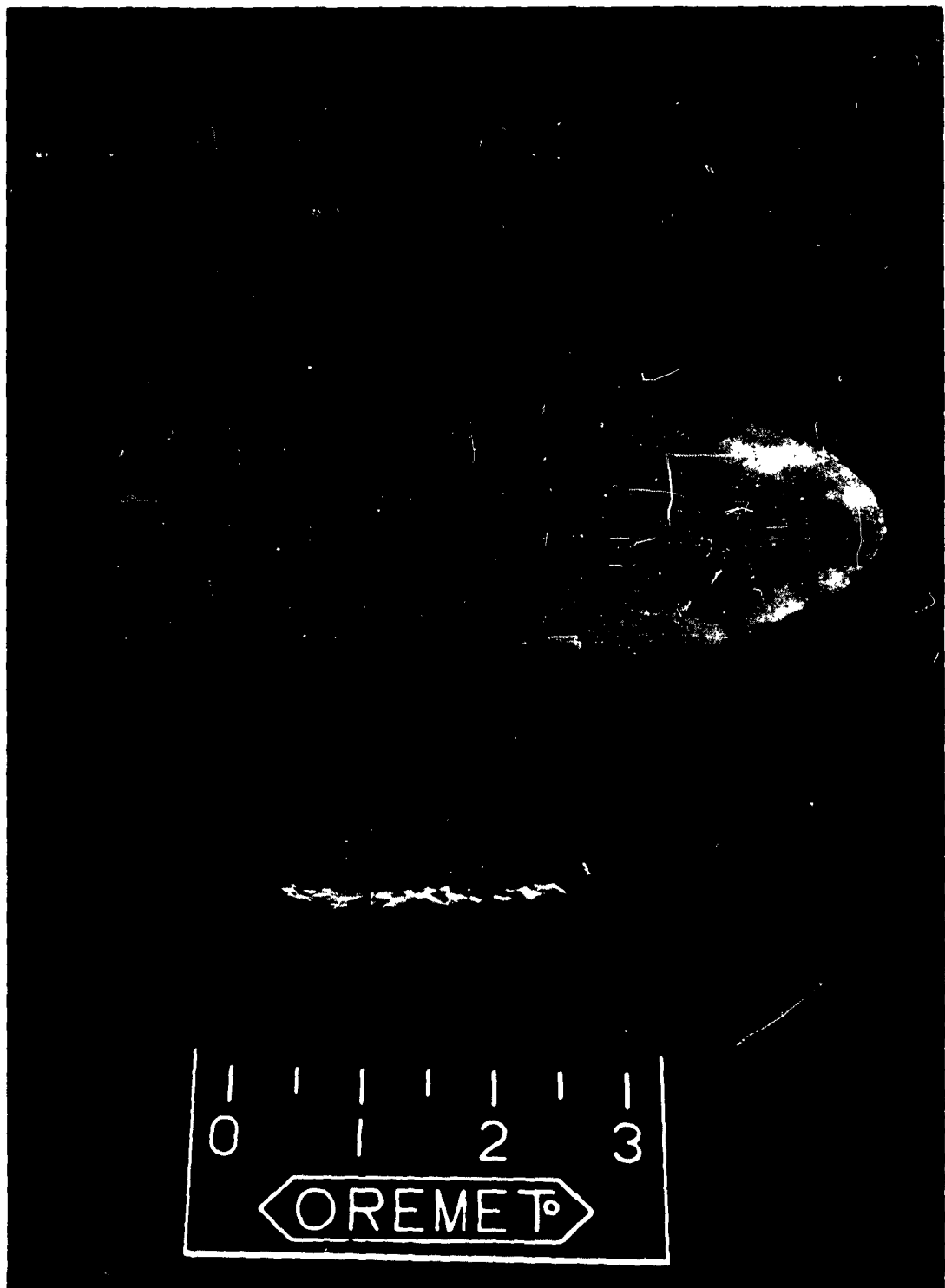
Figure 22

Three Molybdenum Specimens Hot Rolled from 0.625" from
As-Cast Ingots at 1000°C:
          Top Specimen 0.625" to 0.025"
          Middle Specimen 0.625" to 0.079"
          Bottom Specimen 0.625" to 0.235"

Figure 23
Molybdenum Sheet (as rolled) Rolled at 1000°C from 0.625"
to 0.100" and Rolled at Room Temperature from 0.100" to
0.010" from As-cast Ingot Material

IV. SUMMARY OF WORK DONE ON NAVY BUREAU WEAPONS CONTRACT NOw-62-0754c

This contract was designed to culminate work on evaluation of molybdenum metal produced by tin reduction of molybdenite. Enough molybdenum metal powder to produce four arc cast ingots from the tin reduction process was produced. Two hundred pounds of molybdenum powder produced was divided into four lots and converted to four ingots. These ingots were then destructively tested for determination of physical properties. In addition, two molybdenum ingots were produced from commercial molybdenum powder and destructively tested to compare physical properties with those of tin reduced molybdenum. One commercial molybdenum control ingot was produced from as-received high quality powder and the other from the same powder lot with a 2% tin addition prior to melting.

Chemistry was run on all six ingots to determine C, O, N, S, and metallic impurities. Specimens for transverse and longitudinal tensile test bars were sawed from each ingot and ten bend test specimens were sawed from each ingot. Material for swaging was sawed from each ingot and all metal capable of being swaged was swaged from 1 11/32" diameter to 0.7" rounds by random length. Both tensile bars and bend test specimens were machined from all rod successfully swaged. Fractographs

OREGON METALLURGICAL CORPORATION

of all six ingots were made to compare with analytical values.

All specimens were tested and all values compared for
evaluation of tin reduced molybdenum produced.

Results of Testing Molybdenum Produced on NOw-62-0754c

A. Analytical Results

Table XI shows a comparison between the starting molyb-
denum powder produced for each tin reduced ingot and molybdenum
powder used for each commercial ingot.

Table XII shows a comparison between consumable arc cast
molybdenum ingots produced from each of the powders in Table XI.

B. Tensile Testing of As Cast Molybdenum Ingots

Tables XIII, XIV, XV, XVI, XVII, and XVIII show all
tensile test data from all ingots tested. In some cases, extra
tensile bars were machined to further vary testing temperatures
and determine a standard test temperature for pulling bars.
Bend tests proved unreliable for this purpose. All tensile
bars were standard 0.252" diameter shoulder end specimens.

C. Bend Testing of As Cast Molybdenum Ingots

These tests were very disappointing. Results were not
meaningful and were unreliable. Dimensions for specimens were

OREGON METALLURGICAL CORPORATION

TABLE XI

Analytical Values on Molybdenum Powder Used for Each Ingot Melted on this Project, in PPM

	C	O	N	S	Fe	W	Cu	Sn	Cr	Ni	Si	Al
Tin Red. Powder Mo-1	900	140	<10	2000	>1000	<100	>1000	2%	<50	<50	50	80
Tin Red. Powder Mo-2	130	55	<10	670	>1000	<100	>1000	2%	>1000	>1000	400	80
Tin Red. Powder Mo-3	210	90	<10	510	>1000	350	>1000	2%	>1000	>1000	50	50
Tin Red. Powder Mo-4	50	120	<10	450	>1000	<100	>1000	2%	<50	<50	50	50
Comm. Powder Mo-5	30	270	<10	<10	<50	30	<50	<50	<50	<50	50	50
Comm. with tin Mo-6	30	270	<10	<10	<50	50	<50	<50	<50	<50	50	50

TABLE XII

Analytical Values on Each Molybdenum Ingot Produced, In PPM

	C	O	N	S	Fe	W	Cu	Sn	Cr	Ni	Si	Al	H
Tin Red. Ingot Mo-1	700	100	50	10	100	3100	<50	50	<50	<50	50	<50	2
Tin Red. Ingot Mo-2	55	<20	<10	<10	1000	340	<50	<50	<50	<50	<50	<50	-
Tin Red. Ingot Mo-3	70	<20	<10	<10	600	600	<50	<50	<50	<50	<50	<50	-
Tin Red. Ingot Mo-4	<20	90	<10	<10	300	9000	<50	<50	<50	<50	<50	<50	-
Comm. Ingot Mo-5	130	<20	20	<10	100	<100	<50	<50	<50	<50	<50	<50	<1
Comm. with tin Mo-6	<20	130	<10	<10	100	<100	<50	50	<50	<50	<50	<50	-

TABLE XIII

Tensile Test Data on As Cast Ingot Mo-1 from Tin Reduced Molybdenum

	Test Temp., °F	0.2% Offset Yield, PSI	Ultimate, PSI	Elon., % in 4D	% Red. of Area
Transverse*	325	15,760	22,420	0.0	0.0
Transverse	500	14,750	30,510	5.0	6.3
Longitudinal	325	19,600	35,350	4.0	4.9
Longitudinal	500	15,560	33,330	9.5	13.9
Longitudinal	750	14,440	31,920	29.5	49.7
Longitudinal	1000	15,070	34,730	31.0	41.5

*No Test - Broken Outside Gauge Length

TABLE XIV

Tensile Test Data on As Cast Ingot Mo-2 from Tin Reduced Molybdenum

	Test Temp., °F	0.2% Offset Yield, PSI	Ultimate, PSI	Elon., % in 4D	% Red. of Area
Transverse	77	30,960	45,620	9.0	13.8
Transverse	325	15,280	36,460	27.0	54.8
Longitudinal*	77	31,110	36,770	2.5	2.4
Longitudinal*	325	16,970	36,360	9.0	11.7

*No Test - Broken Outside Gauge Length

TABLE XV

Tensile Test Data on As Cast Ingot Mo-3 from Tin Reduced Molybdenum

	Test Temp., °F	0.2% Offset Yield, PSI	Ultimate, PSI	Elon., % in 4D	% Red. of Area
Transverse	77	38,290	40,730	1.5	4.1
Transverse	325	12,120	22,220	4.0	7.9
Longitudinal	77	38,090	39,510	1.0	0.8
Longitudinal	325	13,750	30,960	25.0	33.4

TABLE XVI

Tensile Test Data on As Cast Ingot Mo-4 from Tin Reduced Molybdenum

	Test Temp., °F	0.2% Offset Yield, PSI	Ultimate, PSI	Elon., % in 4D	% Red. of Area
Transverse*	325	-	-	-	-

*Specimen broken in fitting bar in holder grips. Extremely Brittle.

TABLE XVII

Tensile Test Data on As Cast Ingot Mo-5 From Commercial Molybdenum

	Test Temp., °F	0.2% Offset Yield, PSI	Ultimate, PSI	Elon., % in 4D	% Red. of Area
Transverse	77	40,700	55,400	7.0	7.9
Transverse	325	12,630	31,770	33.5	67.8
Longitudinal	77	43,790	49,900	4.0	6.3
Longitudinal	325	13,740	29,700	36.5	73.1

TABLE XVIII

Tensile Test Data on As Cast Ingot Mo-6 from Commercial Molybdenum with 2% Tin Additions

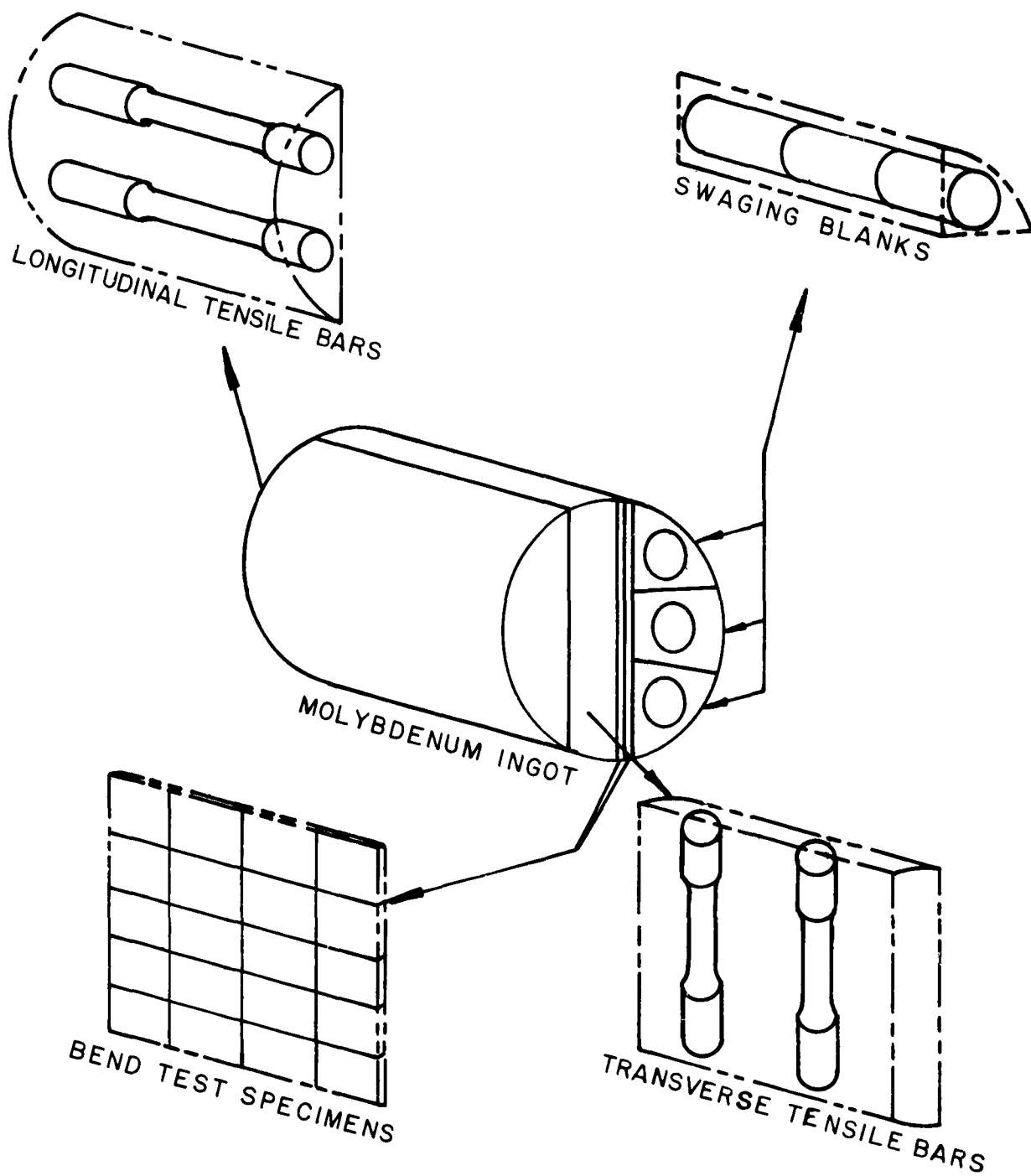|	Test Temp., °F	0.2% Offset Yield, PSI	Ultimate, PSI	Elon., % in 4D	% Red. of Area
Transverse	325	-	5,050	0.0	0.0
Longitudinal	325	10,490	18,330	5.0	6.3
Longitudinal	1000	5,500	16,500	41.0	76.6

taken from those described in the National Materials Advisory

Board documents for evaluation of sheet. If the test specimen

thickness dimension is "T" inches, the width is 12T and the

length is 24T. Test specimen blanks were sawed from ingot

material, milled to rough dimension and then surface lapped

by hand with 120 grit to final dimension.

Ingots Mo-1, Mo-4, and Mo-6 were too brittle to produce

bend specimens. The blanks failed both during sawing and mach-

ining. Grain boundaries were too weak to permit fabrication

of thin specimens. Figure 24 shows the location of sawing to

yield each test ingot specimen, and Tables XIX, XX, and XXI

show all the data on ingots where bend specimens were machined

from ingot blanks.

TABLE XIX

Bend Test Data on As Cast Ingot Mo-2 from Tin Reduced Molybdenum

Thickness, In.	Punch Dia.	Spring Back Angle	Break Before Bending 90°	Temp. °F
0.052	10T	–	Shattered	77
0.052	4T	–	Fractured	300
0.052	4T	–	Fractured	350
0.052	4T	–	Fractured	400
0.052	4T	–	Fractured	450
0.052	4T	–	Fractured	500
0.052	4T	4°	Fractured	600
0.052	4T	2°	Fractured	650
0.052	4T	3°	No Break-Good Test	700
0.052	4T	8°	Fractured	700
0.051	4T	–	Fractured	750
0.051	4T	–	Fractured	800

LONGITUDINAL TENSILE BARS

SWAGING BLANKS

MOLYBDENUM INGOT

BEND TEST SPECIMENS

TRANSVERSE TENSILE BARS

SECTIONING PROCEDURE FOR TEST SPECIMENS

Figure 24

LONGITUDINAL TENSILE BARS

SWAGING BLANKS

MOLYBDENUM INGOT

BEND TEST SPECIMENS

TRANSVERSE TENSILE BARS
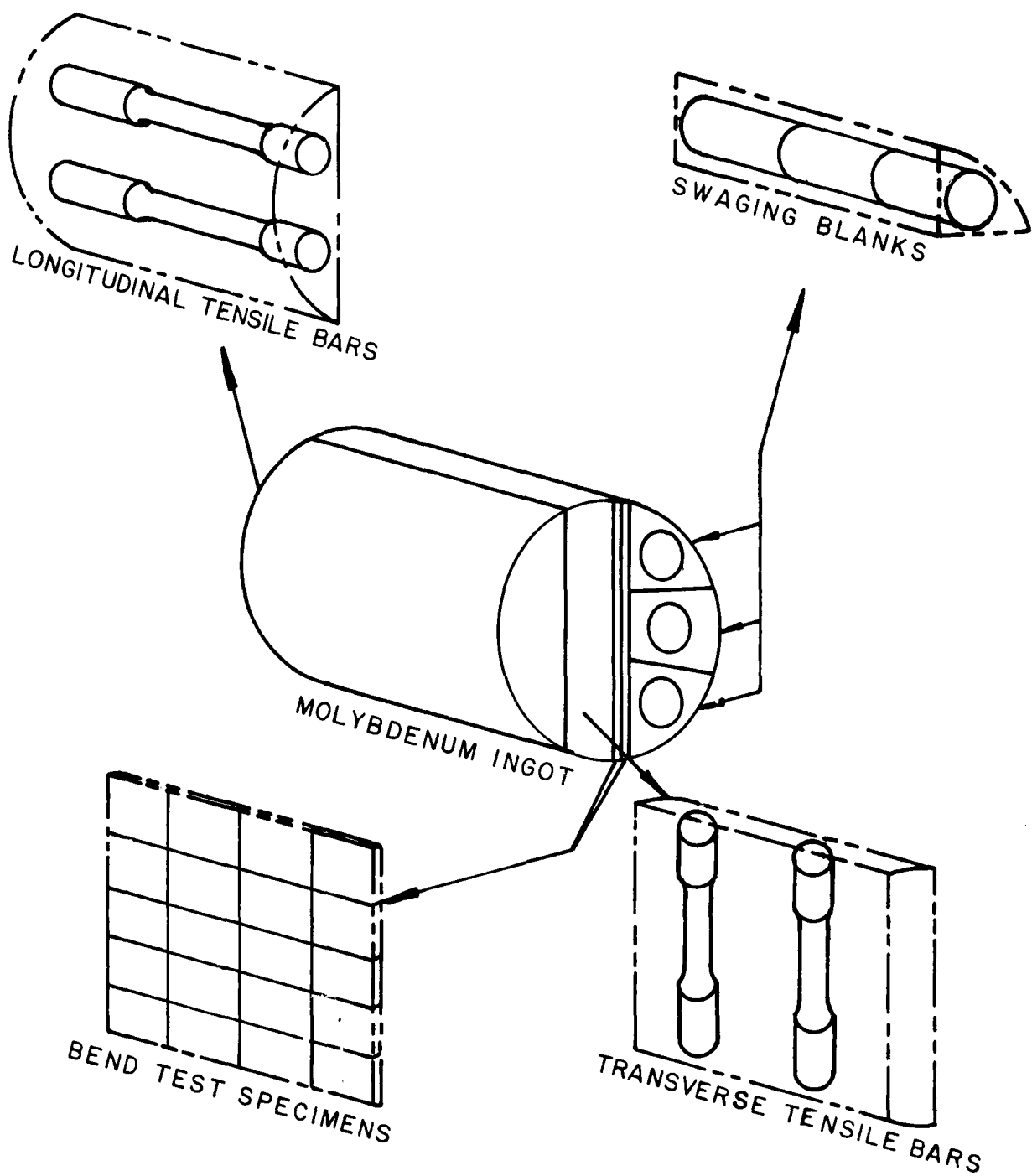
SECTIONING PROCEDURE FOR TEST SPECIMENS

Figure 24

TABLE XX

Bend Test Data on As Cast Ingot Mo-3 from Tin Reduced Molybdenum

Thickness, In.	Punch Dia.	Spring Back Angle	Break Before Bending 90°	Temp °F
0.050	4T	-	Fractured	400
0.050	4T	-	Fractured	450
0.051	4T	-	Fractured	500
0.051	4T	1°	Good Test	500
0.053	4T	-	Fractured	550
0.051	4T	0°	Good Test	550
0.051	4T	1°	Good Test	600
0.050	4T	1°	Good Test	700

(Brittle - Ductile Transition Temperature 500-550°F)

TABLE XXI

Bend Test Data on As Cast Ingot Mo-5 from Commercial Molybdenum

Thickness, In.	Punch Dia.	Spring Back Angle	Bend Before Bending 90°	Temp °F
0.102	10T	-	Fractured	74
0.101	10T	-	Fractured	74
0.103	4T	-	Fractured	300
0.105	4T	-	Fractured	300
0.102	4T	-	Fractured	300
0.105	4T	-	Fractured	300
0.107	4T	1°	Good Test	325
0.104	4T	1°	Good Test	325
0.105	4T	1°	Good Test	350
0.098	4T	0°	Good Test	400

(Brittle - Ductile Transition Temperature 300-325°F)

D. **Tensile Testing and Bend Testing of Swaged Rod from Molybdenum Ingots**

Metal from ingots Mo-1, Mo-3, Mo-4 and Mo-6 could not be swaged successfully. Grain boundaries were too weak to allow

OREGON METALLURGICAL CORPORATION

swaging into rod. Tables XXII, XXIII, XXIV, and XXV show the results of testing specimens of swaged rod from ingots Mo-2 and Mo-5.

TABLE XXII

Tensile Test Data on Swaged Rod from Mo-2, Tin Reduced Molybdenum

Test Temp., °F	0.2% Offset Yield, PSI	Ultimate, PSI	Elong., % in 4D	% Reduction of Area
-10	-	99,370	16.0	16.3
15	-	103,050	11.5	11.6
77	90,430	96,230	19.5	32.8
200	74,950	82,490	25.0	66.8

TABLE XXIII

Tensile Test Data on Swaged Rod from Mo-5, Commercial Molybdenum

Test Temp., °F	0.2% Offset Yield, PSI	Ultimate, PSI	Elong., % in 4D	% Reduction of Area
-10	-	106,460	23.0	23.2
15	-	102,630	20.0	39.6
32	-	101,410	20.0	40.8
77	-	82,020	26.0	40.8
77	82,830	82,830	29.5	51.3
175	63,140	65,170	38.0	65.9
275	57,370	59 390	35.0	68.5

TABLE XXIV

Bend Test Data on Swaged Rod from Mo-2, Tin Reduced Molybdenum

Thickness Inches	Punch Diameter	Spring Back Angle	Break Before Bending 90°	Temperature, °F
0.042	10T	-	Fractured	77
0.042	4T	6°	Fractured	300
0.040	4T	7°	Good Test	325
0.040	4T	6°	Good Test	350

(Brittle - Ductile Transition Temperature 300-325F)

OREGON METALLURGICAL CORPORATION

TABLE XXV

Bend Test Data on Swaged Rod from Mo-5 Commercial Molybdenum

Thickness Inches	Punch Diameter	Spring Back Angle	Break Before Bending 90°	Temperature °F
0.044	9T	–	Fractured	77
0.042	10T	–	Fractured	77
0.044	4T	–	Fractured	200
0.042	4T	0°	Good Test	225
0.043	4T	0°	Fractured	225
0.042	4T	2°	Good Test	250
0.045	4T	6°	Good Test	275
0.042	4T	8°	Good Test	300

(Brittle – Ductile Transition Temperature 225 - 250°F)

E. Hardness Testing of Ingots and Swaged Rods

      Rockwell B hardness was taken on all samples of ingot and swaged rod produced. These values are shown in Table XXVI.

TABLE XXVI

Hardness of Molybdenum Metal Produced

	R_b
Ingot Mo-1	72
Ingot Mo-2	75
Ingot Mo-3	72
Ingot Mo-4	71
Ingot Mo-5	83
Ingot Mo-6	78
Swaged Rod* Mo-1	88
Swaged Rod Mo-2	90
Swaged Rod Mo-5	92

*Portion of rod not large enough for testing but not cracked.

OREGON METALLURGICAL CORPORATION

F. Photographs

The following series of pictures were taken during the project period and are included as supplemental information to illustrate results presented. They are self-explanatory. A fractograph of each ingot is included along with various macro-photos of pulled tensile bars and fractured bend test specimens.

Figure 25
Fractograph of Mo-1, 400X
C=700 PPM, O=100 PPM
(Big Carbides)

Figure 26
Fractograph of Mo-2, 400X
C=55 PPM, O=20 PPM
(Small Carbides Surrounded by Oxide)

Figure 27
Fractorgaph of Mo-3, 400X
C=70 PPM, O=20 PPM
(Few carbides Coated With
Reddish Layer of Oxide)

Figure 28
Fractograph of Mo-4, 400X
C=20 PPM, O=90 PPM
(Few Carbides Coated With
Reddish Layer of Oxide)
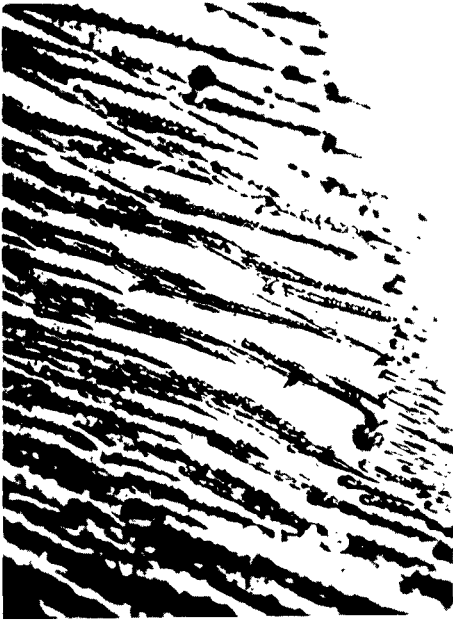
Figure 29
Fractograph of Mo-5, 400X
C=130 PPM, O=20 PPM
(Carbides with Slight
Reddish Hue Around Them)
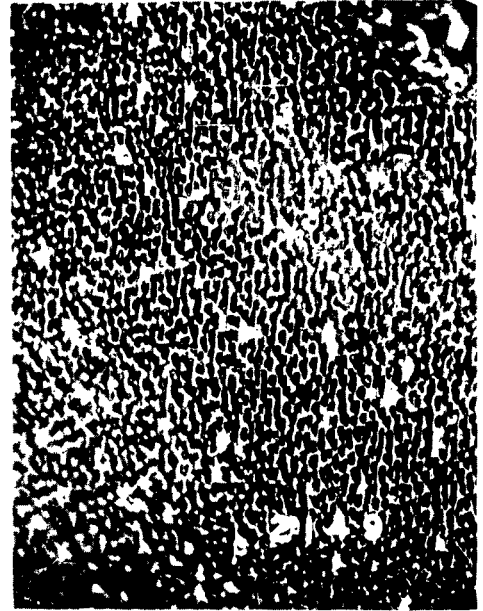
Figure 30
Fractograph of Mo-6, 400X
C=20 PPM, O=130 PPM
(Red Sheet Oxide)
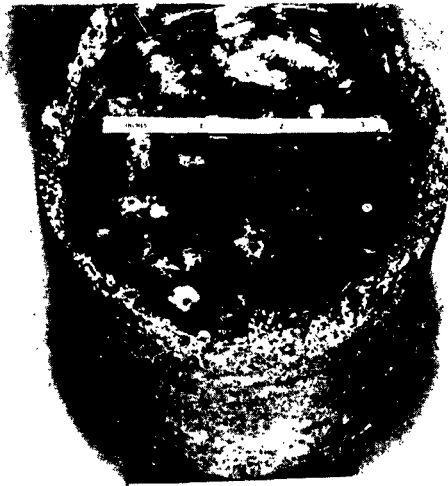
Figure 31
Macrophotograph of Ingot Mo-2, Tin Reduced Molybdenum

D80͘7   Mo2 MT-225   Unalloyed Mo

INCHES   1   2   3
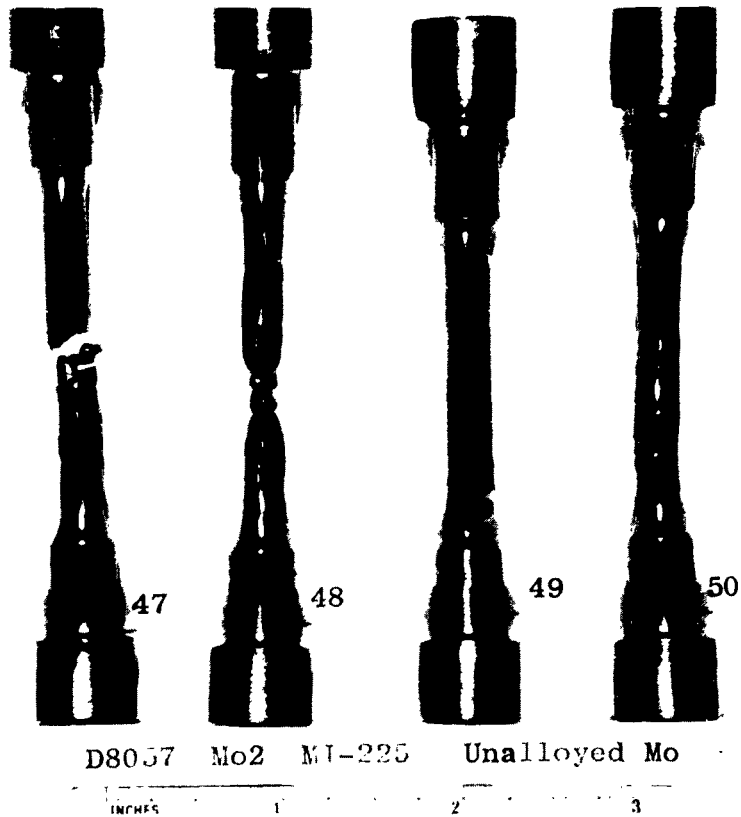
Figure 32
Pulled Tensile Bars from As Cast Molybdenum Ingot Mo-2

SWAGED ROD FROM MOLYBDENUM   INGOT Mo-2
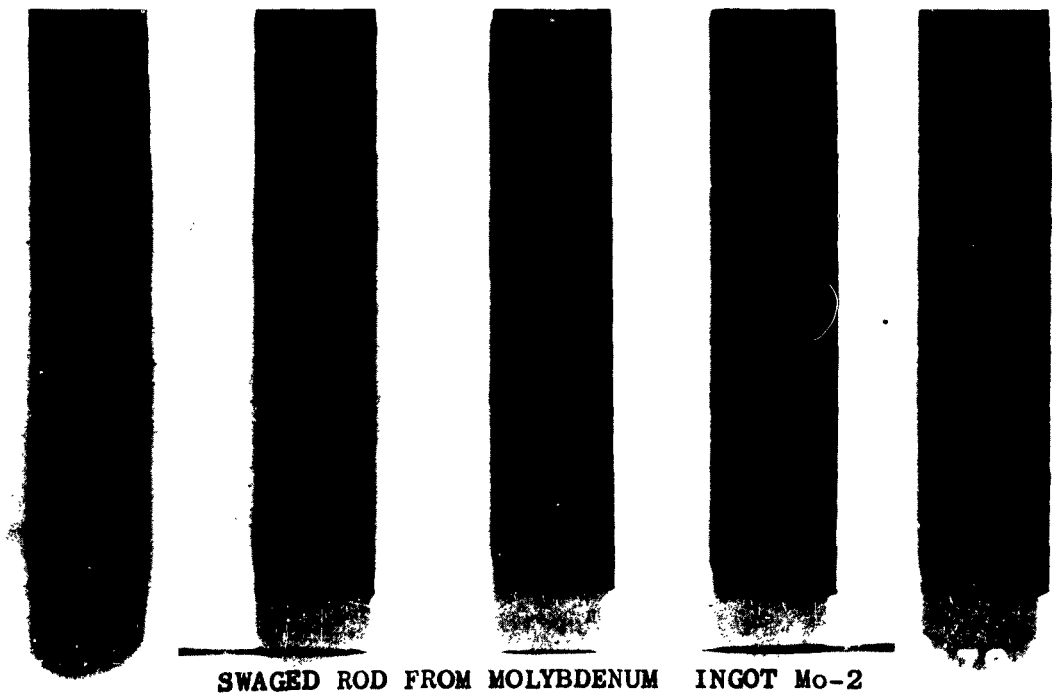
Figure 33
As Swaged Blanks from Molybdenum Ingot Mo-2 for Tensile Bars
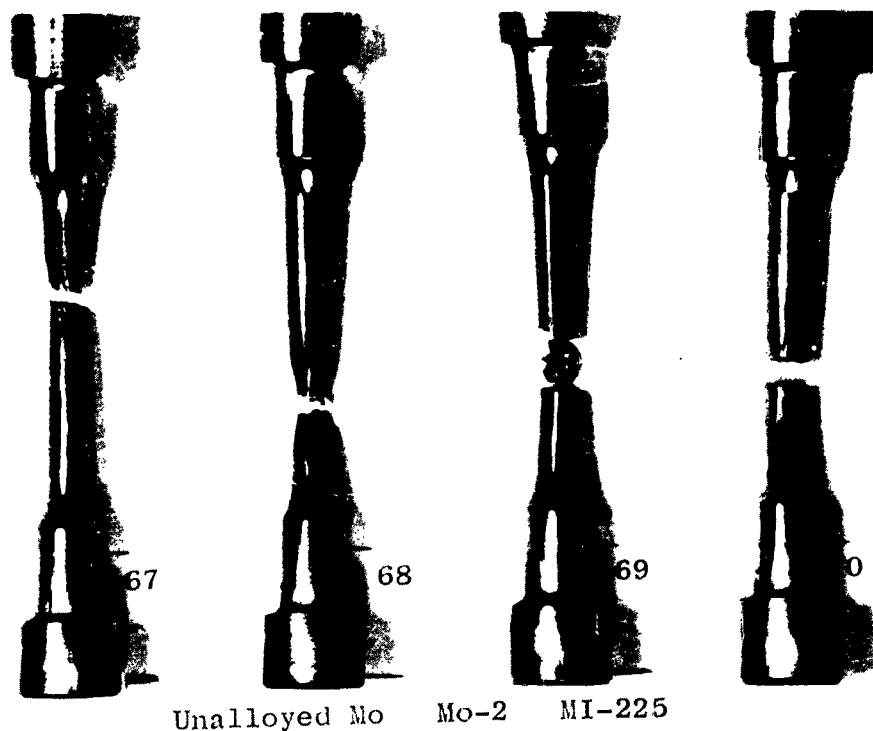
Figure 34
Pulled Tensile Bars from Swaged Rod from Molybdenum Ingot Mo-2
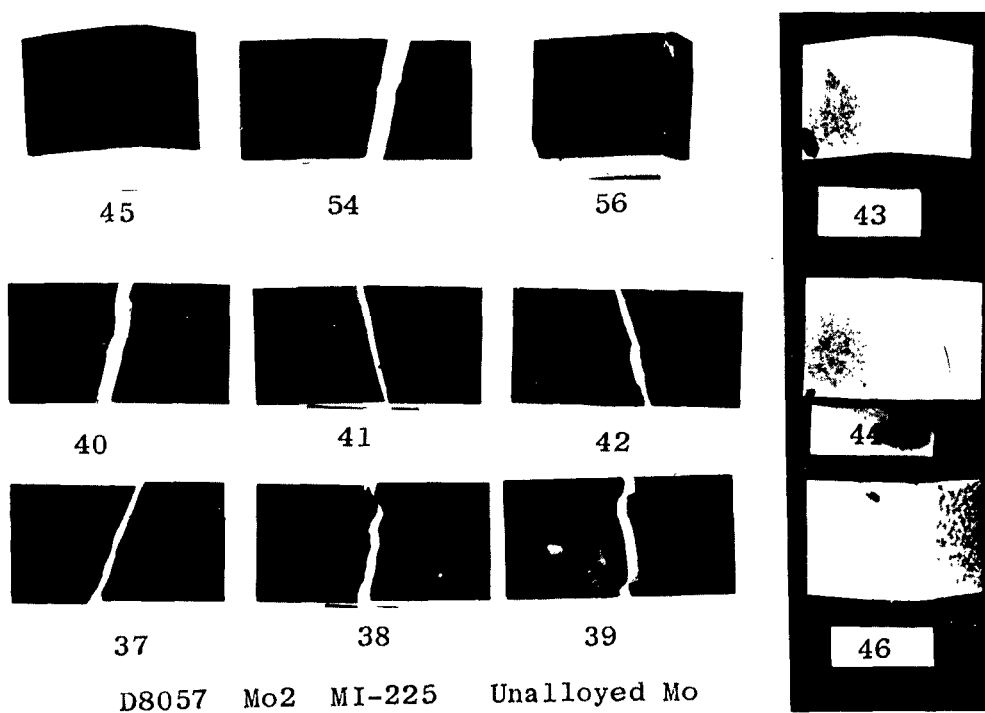
Figure 35
Bend Test Specimens from As Cast Ingot Mo-2 After Testing
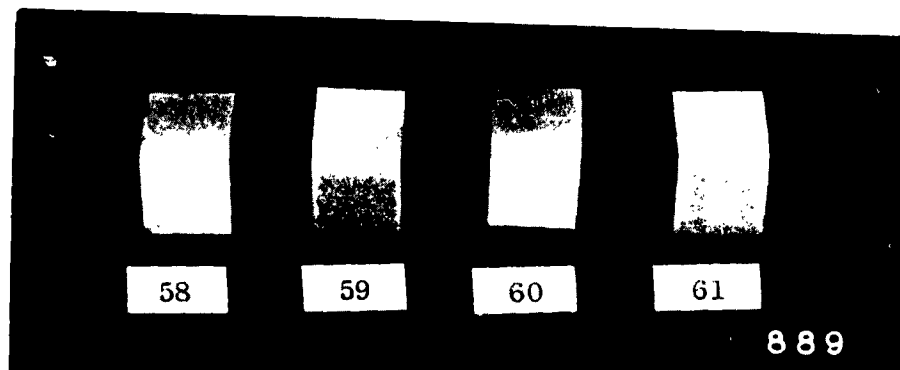
D8057 Mo2 MI-225 Unalloyed Mo
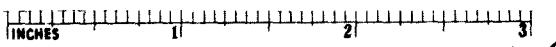
Figure 36
Bend Test Specimens from Swaged Rod from Mo-2 After Testing

Unalloyed Mo   Mo-4   Unalloyed Mo   Mo-3   MI-225
MI-225-71
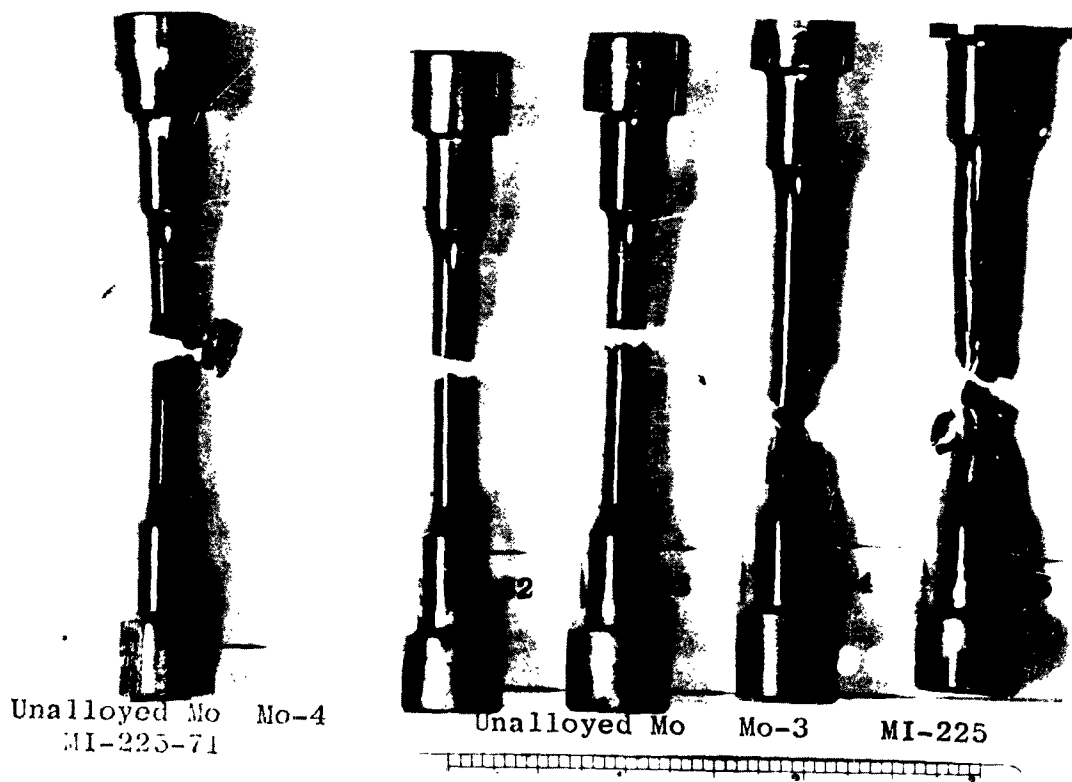
Figure 37
Pulled Tensile Bars from As Cast Ingots Mo-3 and Mo-4
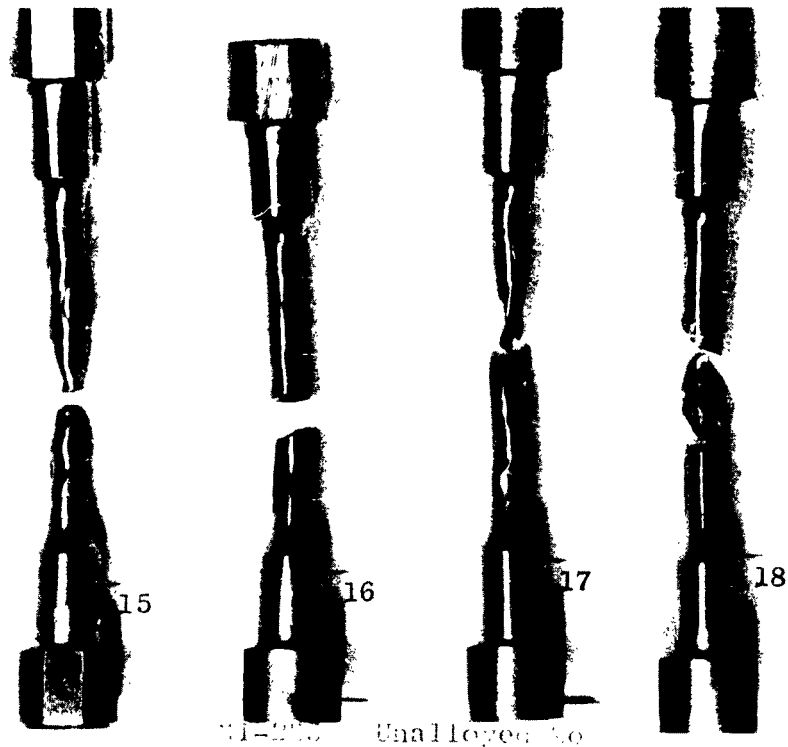
Figure 38
Pulled Tensile Bars from As Cast Commercial Molybdenum Ingot Mo-5

Figure 39
Pulled Tensile Bars from Swaged Rod from Molybdenum Ingot Mo-5
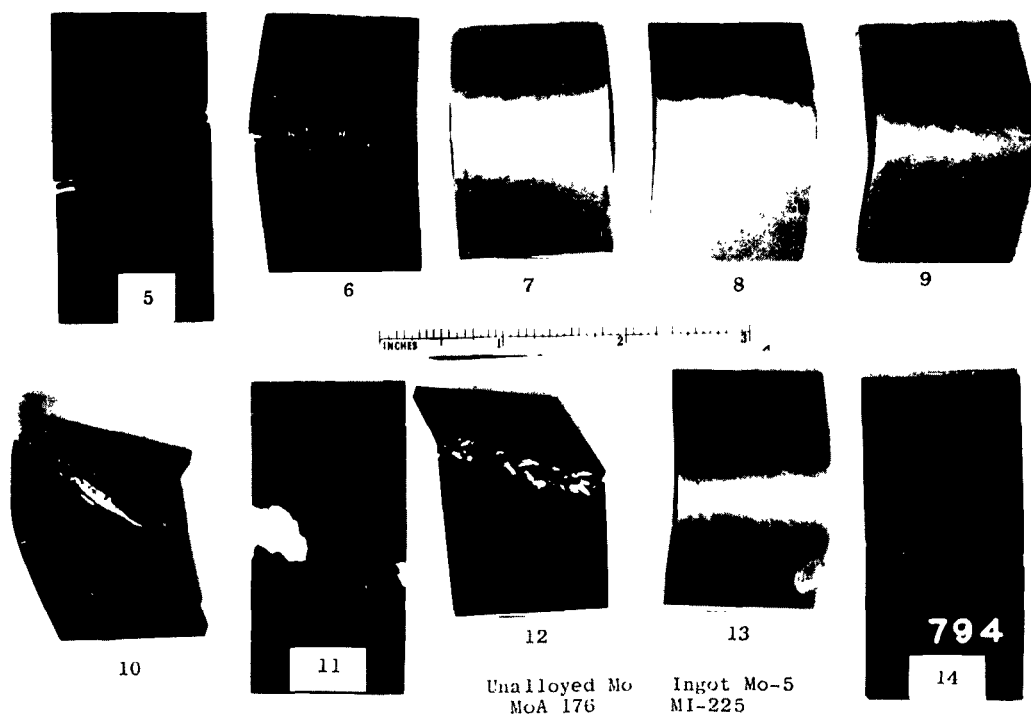
Figure 40
Bend Test Specimens from As Cast Commercial Ingot Mo-5 After Testing
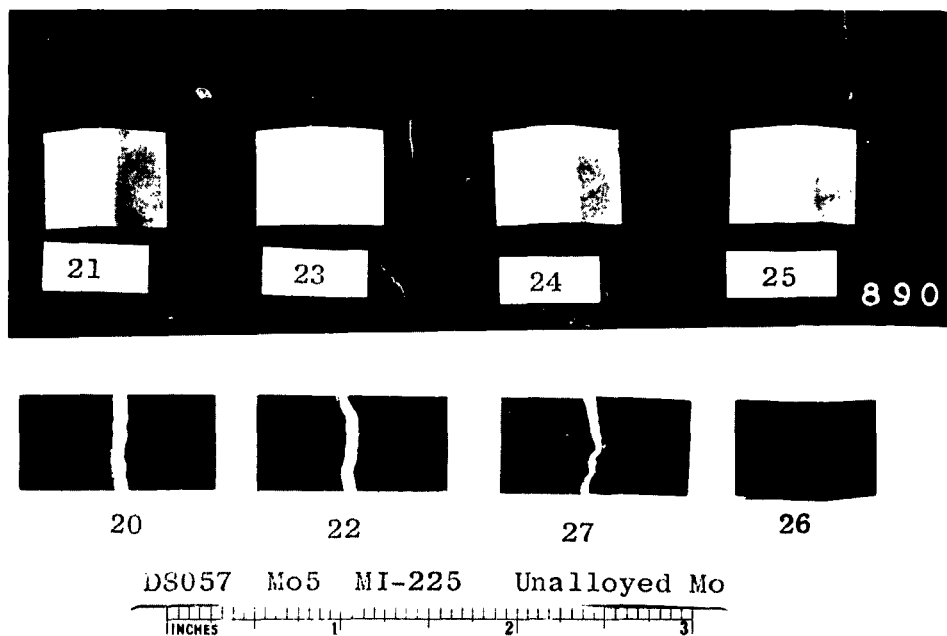
Figure 41
Bend Test Specimens from Swaged Rod from Commercian Ingot Mo-5

G. Graphs

The following two graphs compare ultimate tensile test data and elongation data accumulated on all ingot and swaged rod tested. Figure 24 is a diagram of the sectioning procedure used to saw ingots for test pieces.

GRAPHICAL PRESENTATION OF ULTIMATE STRENGTH TENSILE TEST
DATA FOR ALL INGOTS AND SWAGED ROD TESTED ON THIS PROJECT

NOTE: Mo-1 CONTAINED 700 ppm CARBON AND BECAME STRONGER
AT ELEVATED TEMPERATURES.

Mo-2 SWAGED ROD

Mo-5 SWAGED ROD

Mo-5 INGOT

Mo-3 INGOT

Mo-2 INGOT

Mo-1 INGOT (NOTE)

Mo-6 INGOT

TENSILE TEST TEMPERATURE, °F

ULTIMATE STRENGTH, KSI
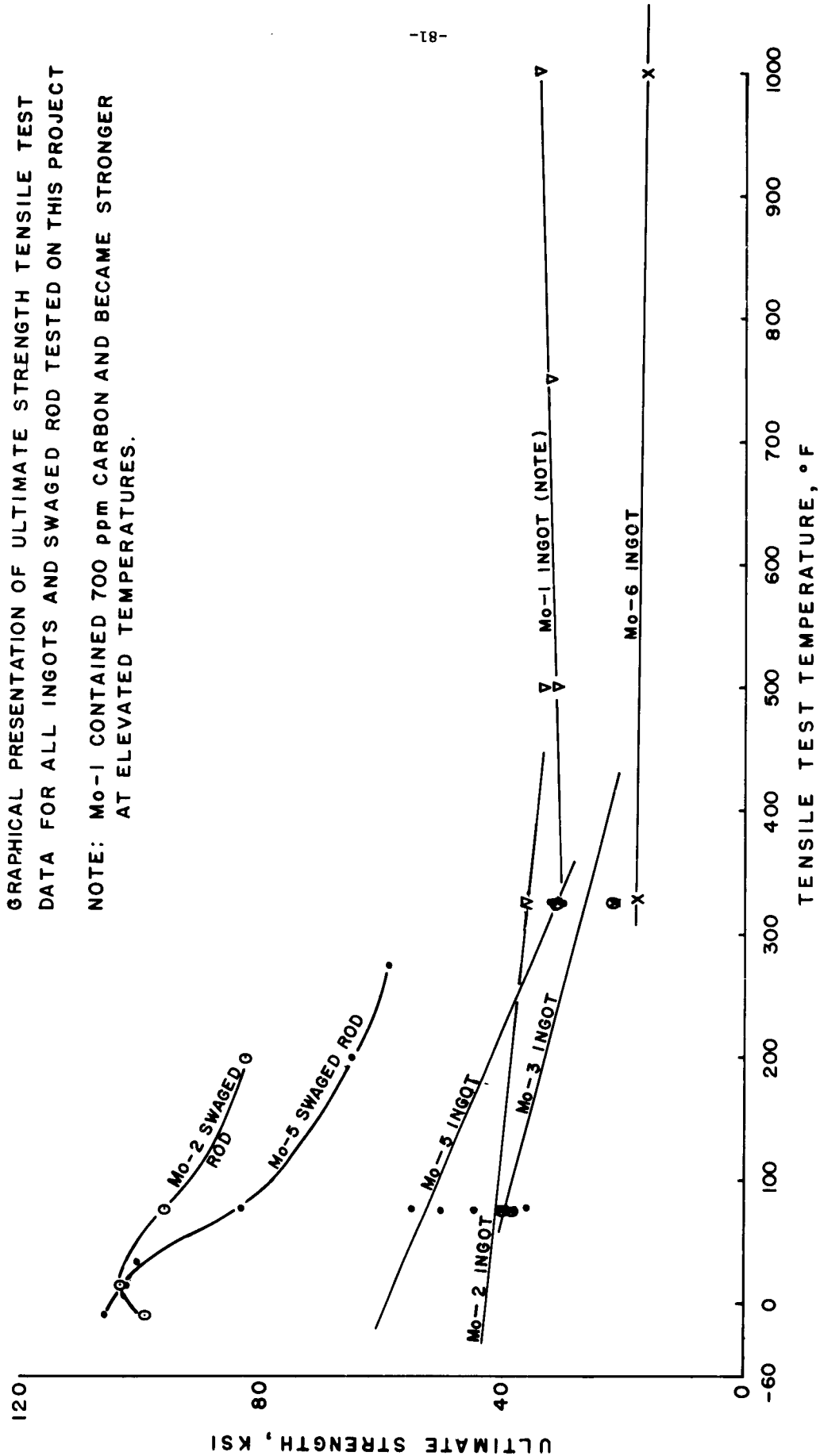
GRAPHICAL PRESENTATION OF TENSILE BAR ELONGATION TEST DATA
FOR ALL INGOTS AND SWAGED ROD TESTED ON THIS PROJECT

-82-
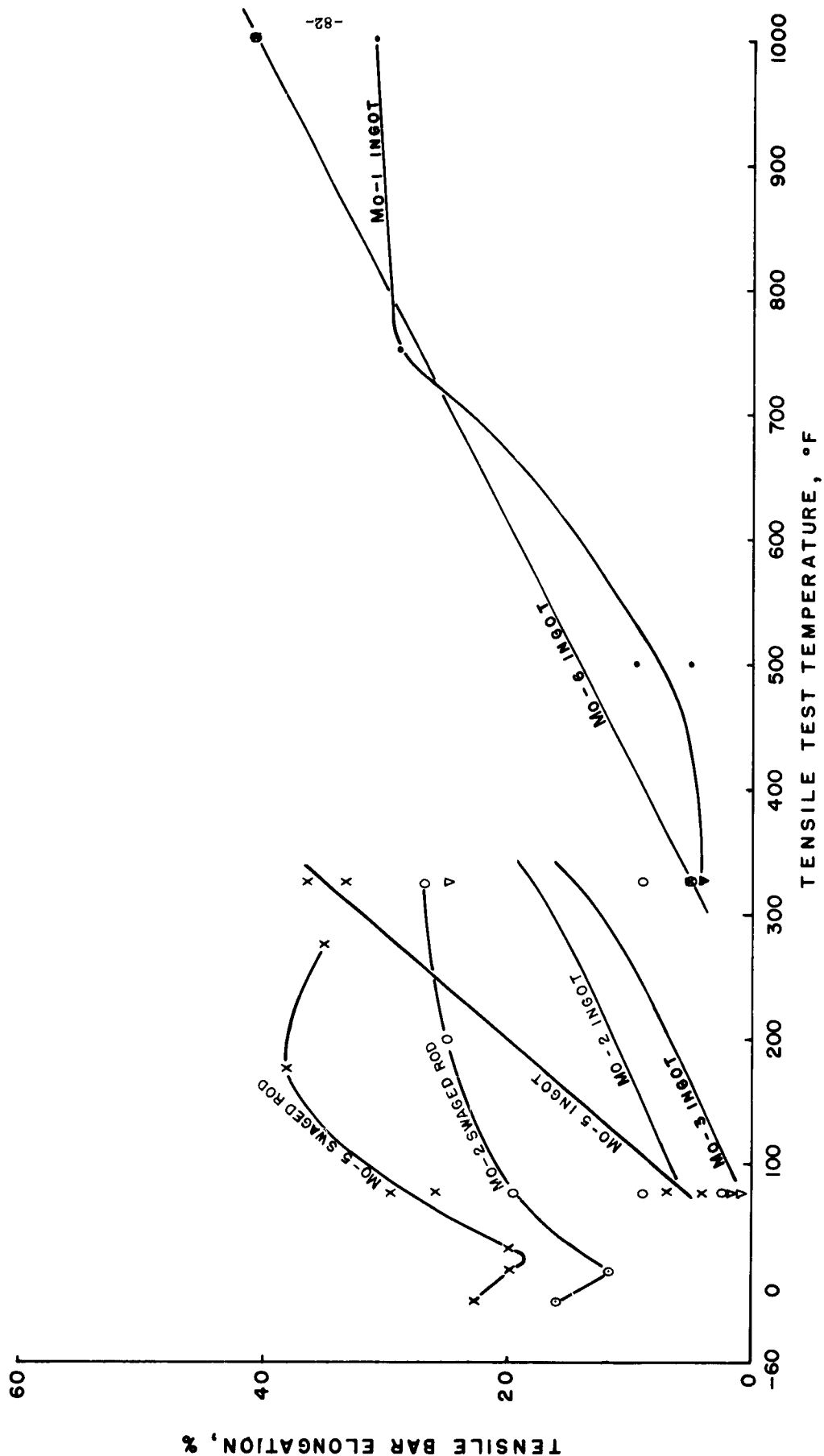
7. EVALUATION AND DISCUSSION OF RESULTS OF WORK DONE ON CONTRACT
NOw 62-0754c

Several basic assumptions were used when beginning work
on this new contract based on prior processing experience.

1. An argon atmosphere system would perform as well
as hydrogen in the tin reduction of molybdenite system.

2. Climax Grade I molybdenite would be amenable to
purification procedures outlined in prior work and would yield
a lower gangue mineral contamination than Kennecott Grade II
molybdenite used previously in most of the early work.

3. All reduction parameters would remain unchanged
by using Climax Grade I molybdenite in place of Kennecott
Grade II molybdenite used in most of the early work.

4. The purification train would perform equally well
whether Climax Grade I molybdenite or Kennecott Grade II molyb-
denite was used in reduction.

5. Climax Grade I molybdenite concentrate being very
low in metallic impurities should allow production of molybdenum
powder low in metallic impurities making conversion to ingot
much easier.

The decision to use argon for the furnace atmosphere

gas on this project rather than hydrogen was made for two reasons. In the last contract we had tried inert gas furnace atmosphere and found no apparent difference on reduction conditions. Also, the funds on this project were such that operations were limited to a one-shift operation, five days a week. This meant that the furnace must be maintained at temperature 24 hours a day, 7 days a week, with very little operator attendance. For reasons of safety, it was deemed necessary to use an argon system in preference to hydrogen.

After reduction of molybdenite for ingot Mo-1, it became apparent that hydrogen had to be added to the system when Climax molybdenite was used as feed material. Furnace element life was erratic and high carbon molybdenum metal was produced. Presumably, flotation oils were present in Climax molybdenite after purification and would crack and form both fixed carbon and carbon containing gas species.

From mass spectrometer gas analysis studies done previously, 4-carbon hydrocarbons, carbon dioxide, and carbon monoxide are formed in this process and are the primary carbon containing species present in the furnace atmosphere system when the purification train becomes saturated. Thus, clean MoS_2 briquettes and furnace elements could unknowingly be placed in a carbon containing atmosphere. This must have been the case for molybdenum powder for control ingot Mo-5 contained

OREGON METALLURGICAL CORPORATION

30 ppm carbon and 270 ppm oxygen prior to melting and 130 ppm carbon plus <20 ppm oxygen after consumable arc melting conversion. All electrode powder compacts were sintered at about 1400°C overnight in the reduction furnace. This is the only place in processing where carbon could have been introduced into the control ingot. This sintering was done in the period of time when the 700 ppm carbon experimental ingot, Mo-1, was produced. To minimize the damage to molybdenum from MoS_2 briquettes, hydrogen had to be added to the system. This would allow minimum cracking to occur.

Since the first ingot produced contained 700 ppm carbon, it was quite apparent that molybdenite being used contained carbon. Climax Grade I molybdenite was not amenable to purification procedures outlined in prior work. This was the root of our problem. Carbon remaining in molybdenite had to be either fixed carbon or residual oils of flotation which were quite insoluble in commercial solvents. If the carbon were present primarily as heavy fuel oil, a hydrogen atmosphere distillation would have to be done to remove the oil without formation of fixed carbon. Our experience has shown that distillation of these particular oils in an atmosphere other than hydrogen causes cracking and formation of fixed carbon as an impurity. If the carbon were present primarily as fixed carbon, an oxidizing atmosphere must be used to remove carbon as a

OREGON METALLURGICAL CORPORATION

gas. A logical choice for further purification was wet hydrogen because both fixed carbon and fuel oils, if present, would be removed in one operation.

All of the molybdenite was run through a wet hydrogen atmosphere at about 750°C. A 30 CFH flow of hydrogen was sparged through water held at 75°C and on through the molybdenite reactor retort exhausting through a 3 PSIG pop-off valve. At this temperature oils were removed by distillation. However, scaling of the stainless steel reactor was noted. After this treatment the molybdenite was thoroughly mixed and a one-pound sample taken. This sample was briquetted with tin and reduced to metal. Carbon on this sample was about 300 ppm (900 ppm carbon on powder for Mo-1).

The wet hydrogen treatment was removing carbon so a second wet hydrogen run was made on all molybdenite. After this treatment, carbon levels were 50 ppm or less on reduced molybdenum metal samples tested. However, prolonged usage of the stainless steel retort with wet hydrogen had caused severe scaling to occur with substantial quantities of non-magnetic scale found abraded into molybdenite processed. This new problem was unexpected. Unless the scale could be completely removed, the advantage of using low metallic impurity Grade I Climax molybdenite would be lost. It is unfortunate that a magnetic stainless steel was not chosen for this processing

OREGON METALLURGICAL CORPORATION

retort. All molybdenite was carefully sifted through a 60 mesh
Tyler Sieve to remove the bulk of the stainless steel scale.
A 55 gallon drum mixer was fabricated and the entire lot of
molybdenite tumbled on ball mill rolls 24 hours so that a
representative sample could be taken. One pound of this con-
centrate was acid leached in a beaker using conditions identi-
cal to those used previously in processing 100 pound batches.
Analysis of this material, when converted to metal, showed
carbon levels less than 50 ppm, but chromium, iron, and nickel
present in concentrations from 0.1% to 0.3%. Releaching did not
lower these metallic impurities appreciably. The advantage of
using Grade I molybdenite had been lost. Since these metallic
impurities should distill from molybdenum metal in arc melting
and carbon was removed to a reasonable level the decision was
made to convert all molybdenite to metal.

Unfortunately, by this time, we were in the carbon-
oxygen system trap with unknown areas of concern in regard to
molybdenite feed. By introducing an oxidizing environment on
the molybdenite to remove carbon, undoubtedly oxides of other
elements present would have been formed. The degree of ser-
iousness of the molybdenite contamination after acid leaching
was not known, but at this point it was recognized that
Kennecott Grade II molybdenite used in early work would have
been a better choice, for we had more experience in purifying
this material. The oils of flotation were easily removed

OREGON METALLURGICAL CORPORATION

leaving no carbon problem. The objectionable gangue minerals containing oxides were particularly hard to remove but could be lowered to tolerable levels in vendor's equipment outside our plant followed by acid leaching. While seemingly purchasing the best molybdenite available for this final evaluation, it turned out that this furnace feed material was somewhat less pure after processing than Kennecott Grade II molybdenite produced earlier and required more effort in purification.

Since the wet hydrogen purification of Climax Grade I molybdenite added unknown levels of oxygen, a series of tin reduction runs were made using full size briquettes. Button samples were melted of each for evaluation. Carbon and oxygen values were monitored and varied up to 50 ppm oxygen and 50 ppm carbon, with most values lower than 50 ppm. On this basis, all molybdenite was converted to metal.

It was found difficult to maintain consistently low tin levels in reduced molybdenum metal after adding 10% by volume hydrogen to the system. Apparently, the amount of hydrogen reduction during tin reduction was significant enough to throw off the tin balance. Since we had no way of continuously monitoring hydrogen consumption, the quantity of hydrogen present at any one time would vary due to the amount used during the hydrogen reduction of molybdenum sesquisulfide side reaction. Make-up hydrogen was somewhat

OREGON METALLURGICAL CORPORATION

arbitrarily added from time to time to offset usage. This
being the case, we were never able to achieve a complete tin
reduction without having excess tin present. This variance
in tin requirements was not noted in previous work in hydrogen
atmosphere or pure inert gas atmosphere after proper tin re-
quirements were determined.

Physical tests were as disappointing as chemical tests
on molybdenum produced. Molybdenum powder produced contained
appreciable quantities of iron, copper, sulfur, chromium, nickel,
and 2% tin. Carbon and oxygen values were also much higher than
espected, varying from 50 ppm to 200 ppm. While these impurities,
with the exception of iron, were lowered in arc melting conver-
sion to levels comparable to or lower than those achieved in
conversion of commercial molybdenum powder to ingot, the data
shows that powder produced was less pure. In addition, electrode
fabrication was more difficult due to these impurities causing
tungsten pickup at an abnormal level.

Physical testing of tin reduced molybdenum and commercial
molybdenum done shows non-uniform quality metal ingots were
produced. The best metal produced by either method was similar
in physical properties. Both superior ingots, Mo-2 and Mo-5,
could be worked directly from as-cast ingot blanks into swaged
rod quite easily. The ingots had reasonably clean grain
boundaries and good low temperature ductility. In all

OREGON METALLURGICAL CORPORATION

probability metal from either ingot could have been forged
directly from as-cast ingot material as demonstrated in pre-
vious work on small samples of molybdenum.

All of the other ingots had poor strength and ductility.
Grain boundaries were weak and fractographs show gross contam-
ination at grain boundaries. From fractographs Mo-1 contained
gross carbon contamination, and Mo-3, Mo-4, and Mo-6 contained
gross oxygen contamination. This is not borne out in all
cases from analytical results, however.

Ingot Mo-6 was produced from commercial powder (the
same lot used for Mo-5) with 2% tin addition prior to arc
melting conversion into ingot. This level of tin was equiva-
lent to that found in molybdenum powder produced by the tin
reduction process. This ingot was added to determine whether
there is any injurious effects due to excess tin present.
Since sheet oxide was found at grain boundaries in this final
melt ingot, very little was learned. No physical data could
be gathered because of grain boundary weakness. Tin was
removed to very low levels, 50 ppm, in arc melting and ana-
lytically oxygen was at a level commonly encountered in con-
verting molybdenum powder without tin addition.

VI. CONCLUSIONS

Molybdenum metal produced by the tin reduction of molybdenite in pilot plant studies from purified Kennecott Grade II molybdenite at the end of the early work contained less than 50 ppm combined carbon, oxygen, and nitrogen. This metal was superior chemically to commercial molybdenum and could be fabricated easily by hammer forging and rolling in the as-cast condition from ingot material. Some of the Kennecott Grade II molybdenite could be purified easily and some contained substantial quantities of mineral oxides such as spinel which were difficult to remove. Electrostatic separation was effective in lowering these mineral oxides. The oils used in flotation purification of this molybdenite concentrate could be removed easily without cracking, leaving a low carbon concentrate. In most instances, after purification, Kennecott Grade II molybdenite contained substantial quantities of iron and copper, presumably in the form of sulfides. These two impurities were found in molybdenum powder produced by the tin reduction process. During consumable arc casting conversion of this powder, copper was removed by distillation early and was removed quite completely. Iron, however, distilled more slowly and varying quantities from a few parts per million to 0.1% were found in ingots, depending on initial concentrations and number of melts. Both of these impurities

OREGON METALLURGICAL CORPORATION

would slag out on ingot sidewalls and could be removed by flaking on a wire buffing wheel very early. Presumably, they could have been removed faster and more completely by scalping each ingot sidewall prior to remelting. The particle size of Kennecott Grade II molybdenite was larger than other concentrates received, making compaction with tin easier and stronger. Less friable briquettes were made in comparison to other vendors concentrates received. In a pure gas atmosphere, either hydrogen or inert gas, residual tin in reduced molybdenum powder produced by the tin reduction of molybdenite process could be controlled in the neighborhood of 0.1 - 0.2% by weight. Reduction proceeded smoothly at 1300°C - 1350°C and was complete in about 6 hours.

Molybdenum metal produced by the tin reduction of molybdenite in pilot plant studies from purified Climax Grade I molybdenite contained carbon and oxygen in concentrations equivalent to that in commercially available molybdenum metal produced by the hydrogen reduction of molybdenum oxide. This was due to impurities in molybdenite that could not be removed in purification. The flotation oils used in processing this concentrate were different from those found in Kennecott Grade II concentrate and could not be easily removed. Special conditions such as hydrogen atmosphere distillation minimized cracking of flotation oils during distillation, but carbon could not be completely removed by hydrogen distillation even at elevated

OREGON METALLURGICAL CORPORATION

temperatures (750°C). Carbon present either as fixed carbon
in as-received concentrate, fixed carbon from pilot plant
processing in hydrogen atmosphere, or incomplete distillation
of oils at 750°C, was not removed. Wet hydrogen (water vapor
carried in flowing hydrogen gas) treatment of Climax molybdenite
lowered carbon, but this oxidizing environment introduced the
carbon-oxygen system into the tin reduction process. A low
carbon, low oxygen molybdenite was not produced from wet hydro-
gen treatment. In the particular equipment used, wet hydrogen
treatment was further complicated by scaling of the reactor
retort with some abraded stainless steel scale found in purified
molybdenite. This scale could not be removed by methods tried.
In addition to this scale, extensive wet hydrogen treatment did
not remove absolutely all carbon from molybdenite processed.
The end result of processing Climax Grade I molybdenite was
that, while as-received material contained virtually no metallic
impurities along with carbon, the final purified molybdenite
product was contaminated with iron, chromium, nickel, traces of
carbon, and an unknown quantity of oxygen from oxides present.
A process was not evolved to purify this concentrate adequately.
In fact, the end product was not as pure as Kennecott Grade II
molybdenite after processing.

A combined low carbon, low oxygen product (<50 ppm) was
not produced from Climax Grade I molybdenite. As mentioned

OREGON METALLURGICAL CORPORATION

previously, hydrocarbons were being recycled in the purification system precluding formation of low carbon molybdenum. In addition, iron, chromium, and nickel were found in as-produced molybdenum powder in concentrations from 0.1% - 0.3%. These metallic impurities caused difficulty in electrode fabrication resulting in abnormal levels of tungsten pickup in consumable arc cast ingots. Impurities present in arc cast ingots from the tin reduction process using Climax Grade I molybdenite were high enough to preclude their being superior in physical testing to ingots produced from commercially available hydrogen reduced powder. Physical tests performed show that a non-uniform quality product was produced and the best ingot produced was no better than good quality carbon deoxidized commercial molybdenum. All ingots produced from Climax molybdenite were also inferior to the <50 ppm combined carbon, oxygen, and nitrogen ingot produced from Kennecott Grade II molybdenite.

A furnace system of pilot plant dimensions was successfully fabricated to desulfurize molybdenite with tin. The system was automated to run without operator attention indefinitely with the exception of charging and discharging reduction loads in the reaction zone. Reduction temperatures of 1400°C could be maintained easily continuously, and higher temperatures could be achieved if desired. Reduction by

OREGON METALLURGICAL CORPORATION

products from tin desulfurization of molybdenite could be removed effectively continuously in a purification train fabricated to recirculate gas. However, carbon species not removed in purification of Climax Grade I molybdenite could not effectively be removed continuously to low levels. The entire processing outline for the tin reduction of molybdenum disulfide was evolved into a functioning pilot plant program which operated quite smoothly. Operations such as briquetting raw materials, charging the furnace, discharging the furnace, and grinding loosely sintered powder products were performed quite smoothly during Contract NOw-62-0754c.

The final conclusion one can reach is that a low carbon, low oxygen, low metallic impurity molybdenum disulfide reduced with tin in a pure hydrogen or inert gas atmosphere will yield molybdenum metal powder with lower interstitials than commercially available molybdenum produced by the hydrogen reduction of molybdenum oxide. A hydrogen system atmosphere or partial hydrogen inert gas atmosphere was found preferable to inert gas because higher quality metal could be produced from molybdenite containing carbon and oxygen species impurities. Exhausting hydrogen gas to atmosphere would be preferable to recycling in this process to preclude recycling gaseous impurities which may not be removed continuously in a gas purification system. Since the vast majority of time and funds were

OREGON METALLURGICAL CORPORATION

spent on evolving a pilot plant system for reducing molybdenite, and little time spent on purification of molybdenite concentrates in comparison, a pilot plant process for producing ultra-pure molybdenite from all commercially available molybdenite concentrates was not evolved.

Respectfully submitted,

OREGON METALLURGICAL CORPORATION

Charles Krey
Development Engineer

H. Gordon Poole
Technical Director

Stephen M. Shelton
President

DISTRIBUTION LIST

Contract NOw-62-0754-c

Armour Research Foundation
10 West 35th Street
Chicago 16, Illinois

Battelle Memorial Institute
Attn: Defense Metals Info. Center
505 King Avenue
Columbus 1, Ohio

Climax Molybdenum Co. of Michigan
14410 Woodrow Wilson Boulevard
Detroit 38, Michigan

Colorado School of Mines
Research Foundation
Golden, Colorado

Aeronautical Systems Division
Wright-Patterson Air Force Base
Ohio
Attn: ASRCMP

Sylvania Electric Products, Inc.
Chemical & Metallurgical Divn.
Towanda, Pennsylvania

Wah Chang Corporation
P. O. Box 366
Albany, Oregon

Westinghouse Electric Corp.
Metals Plant
Attn: Mr. F. L. Orrell
Blairsville, Pennsylvania

Fansteel Metallurgical Corp.
2200 Sheridan Road
North Chicago, Illinois

National Aeronautics & Space Adm.
1520 H Street, N. W.
Washington 25, D. C.   (3 copies)

Armed Services Technical Information Agency
Arlington Hall Station   (8 copies - released ithout
Arlington, Virginia   restriction)

Bureau of Naval Weapons
Navy Department
Washington 25, D. C.
            DIS-3   (2 copies)
            RMGA-81   (1 copy)
            RRMA-23   (Remaining copies)

FINAL REPORT ONLY

Alloyd Corporation
35 Cambridge Parkway
Cambridge 42, Massachusetts

E. I. DuPont de Nemours & Co.
Pigments Department
Experimental Station
Wilmington 98, Delaware

Temescal Metallurgical Corp.
2850 Seventh Street
Berkeley, California

Reactive Metals, Inc.
Attn: Mr. L. G. McCoy
960 Warren Avenue
Niles, Ohio

OREGON METALLURGICAL CORPORATION

General Electric Co.
Metallurgical Engineering
Applied Research Operation
Flight Propulsion Laboratory Dept.
Attn: Mr. L. P. Jahnke
Cincinnati 15, Ohio

Office of Naval Research
Navy Department
Washington 25, D. C.

Thompson Ramo Wooldridge, Inc.
TAPCO Group
23555 Euclid Avenue
Cleveland 17, Ohio

General Telephone & Electronics
        Laboratories
P. O. Box 59
Bayside, L. I., New York

Watertown Arsenal Laboratory
Watertown, Massachusetts

Aerojet-General Corporation
Solid Rocket Plant
Attn: Mr. A. V. Levy
        Department 4610
P. O. Box 1947
Sacramento, California

Naval Air Material Center
Attn: Aeronautical Matls. Lab.
Philadelphia 12, Pennsylvania

Westinghouse Electric Corp.
Lamp Division
Research Department
Bloomfield, New Jersey

Atomic Energy Commission
Research Division
Germantown, Maryland

OREGON METALLURGICAL CORPORATION

General Electric Co.
Metallurgical Engineering
Applied Research Operation
Flight Propulsion Laboratory Dept.
Attn: Mr. L. P. Jahnke
Cincinnati 15, Ohio

Office of Naval Research
Navy Department
Washington 25, D. C.

Thompson Ramo Wooldridge, Inc.
TAPCO Group
23555 Euclid Avenue
Cleveland 17, Ohio

General Telephone & Electronics
        Laboratories
P. O. Box 59
Bayside, L. I., New York

Watertown Arsenal Laboratory
Watertown, Massachusetts

Aerojet-General Corporation
Solid Rocket Plant
Attn: Mr. A. V. Levy
        Department 4610
P. O. Box 1947
Sacramento, California

Naval Air Material Center
Attn: Aeronautical Matls. Lab.
Philadelphia 12, Pennsylvania

Westinghouse Electric Corp.
Lamp Division
Research Department
Bloomfield, New Jersey

Atomic Energy Commission
Research Division
Germantown, Maryland

OREGON METALLURGICAL CORPORATION